REMARKS / ARGUMENTS

Applicants and their attorney thank the Examiner for his careful examination of the present application after entry of the previously filed Amendment (February 2004). It appears that the Examiner has withdrawn the rejection made in the first Office Action, of Claims 2-6, 9 and 10 under 35 U.S.C. § 112, second paragraph, based on the claim amendments presented in the February 2004 Amendment. New rejections made by the Examiner in the final Office Action, to the amended specification and claims, are addressed below.

Status of Claims

Claims 1 and 7-16 remain pending in the present application. Claims 2-6 were previously cancelled and remain cancelled. Claims 1 and 7-13 are currently under examination, while Claims 14-16 are withdrawn from further examination at this time, pending allowance of one or more generic claims.

Independent Claim 1 has been amended by the foregoing amendments to more clearly recite the novel features of the present invention. More particularly, reference to types of polymerization reactions has been deleted from Claim 1 and the features of original Claim 9 have been incorporated into Claim 1.

In addition, Claim 9 has been amended to recite a specific embodiment of its originally recited subject matter. Claim 10 has been amended by the foregoing amendments to correct a typographical error and clarify its dependency.

Election

As discussed on pages 2-3 of the final Office Action, the Examiner issued a telephonic restriction requirement on April 12, 2004, which required election of one of the following species for further prosecution at this time:

    a.   (Claim 13) – wherein a plurality of soft polymer particles comprise the soft phase in said aqueous dispersion of polymer particles and a plurality of hard polymer particles comprise the hard phase; and

b.   (Claims 14-16) – wherein the polymer particles comprise polymer particles with a soft phase core and a hard phase shell.

Applicants and their attorney hereby confirm election of species "a" (Claim 13) for further prosecution at this time. It is understood that Claims 14-16 are withdrawn from further consideration at this time. Applicants hereby reserve the right to file one or more divisional applications directed to the subject matter of withdrawn Claims 14-16.

Additionally, while the Examiner has stated that Claim 12 of the present application is generic, Applicants believe that each of Claims 1 and 7-12 are generic to both species (a and b) identified by the Examiner. Thus, Claims 1 and 7-13 are believed to be under examination at this time. Applicants further understand that if any generic claim is found to be allowable, Applicants will also be entitled to examination of the withdrawn claims (i.e., Claims 14-16).

Objection to the Specification Under 35 U.S.C. 132

On page 4 of the final Office Action, the Examiner has objected to the amended specification, under 35 U.S.C. § 132 because the Examiner believes that certain material added by the February 2004 Amendment was not supported by the specification as filed.

More particularly, the Examiner has determined that the following amended language was unsupported by the original, as-filed specification, and is, therefore, new matter and not permissible:

(Specification paragraph beginning at page 11, line 27)

In the process for making the polymeric additive compositions, the types of polymerizations that may used to form the polymeric additive compositions include <u>conventional or "classical"</u> emulsion (gradual addition/shot), <u>miniemulsion,</u> solution, <u>and</u> bulk, <u>and any of these types of polymerization may proceed through the reaction mechanisms of</u> radical chain (addition) or step reaction (condensation). Typically, free-radical

emulsion polymerization is used as it readily forms polymer particles that can have a range of morphologies.

In addition, the Examiner has determined that the additional text that was added to Example 5 of the specification are also new matter, and not permissible under 35 U.S.C. § 132, because the procedures described in the additional text are not found in the original specification.

It is respectfully submitted that the neither of the aforesaid amendments to the specification constitute new matter because they each merely clarified that which was already known and understood by persons of ordinary skill in the art based upon the original language of that passage and the general knowledge in the art.

There is abundant caselaw on the issue of whether amendments to the specification or claims of a patent application introduce new matter prohibited by 35 U.S.C. § 132, as well as the standards by which the issue of new matter is to be analyzed and judged. Compliance with the written description requirement is a question of fact which must be resolved on a case-by-case basis. Vas-Cath, Inc. v. Mahurkar, 935 F.2d at 1563, 19 USPQ2d at 1116 (Fed. Cir. 1991). "[T]he PTO has the initial burden of presenting evidence or reasons why persons skilled in the art would not recognize in the disclosure a description of the invention defined by the claims" In re Wertheim, 541 F.2d 257, 263, 191 USPQ 90, 97 (CCPA 1976).

Fundamentally, "[t]he function of the description requirement is to ensure that the inventor had possession, as of the filing date of the application relied on, of the specific subject matter later claimed by him." In re Wertheim, 541 F.2d 257, 262, 191 USPQ 90, 96 (CCPA 1976); see also, Moba, B.V. v. Diamond Automation. Inc., 325 F.3d 1306, 1319, 66 USPQ2d 1429, 1438 (Fed. Cir. 2003); and Vas-Cath, Inc. v. Mahurkar, 935 F.2d 1555, 1563, 19 USPQ2d 1111, 1116 (Fed. Cir. 1991).

The court holdings make clear that information which is conventional or well-known to persons of ordinary skill in the art need not be described in detail in

the specification. See, e.g., Hybritech, Inc. v. Monoclonal Antibodies, Inc., 802 F.2d 1367, 1379-80, 1384, 231 USPQ 81, 90, 94 (Fed. Cir. 1986); and Martin v. Johnson, 454 F.2d 746, 751, 172 USPQ 391, 395 (CCPA 1972) (the description need not be in *ipsis verbis* [i.e., "in the same words"] to be sufficient to satisfy the adequate description requirement). Furthermore, long-standing caselaw established that where amendments by the applicant simply amplified or restated descriptive matter so as to provide a more clear and complete explanation, then no new matter has been added. See, Westinghouse Electric & Mfg. Co. v. Radio Corp. of America, 24 F.Supp. 933 (D.C.Del. 1938). Thus, mere rephrasing of a passage does not constitute new matter and rewording a passage where the same meaning remains intact is permissible. In re Anderson, 471 F.2d 1237, 176 USPQ 331 (CCPA 1973).

The courts have also explained that an amendment is not new matter where it is merely elaboration, designed to explain and make more clear that which was already reasonably indicated by the original specification to be within the scope of the invention. Proctor & Gamble Mfg. Co. v. Refining, Inc., 135 F.2d 900, 904, 57 USPQ 505 (4th Cir. Va., 1943) (amendments to the specification which added 3 new paragraphs in which process steps and conditions of the inventive process were clarified were found not to constitute new matter because the court found that the steps and conditions had already been clear to persons of ordinary skill in the art based upon the original disclosure and the general knowledge in the art at the time).

With respect to the statutory requirement that no amendments may introduce new matter into the disclosure of an invention, the fundamental inquiry is whether the material added by amendment was inherently contained in the original application; thus, to avoid the new matter prohibition, an applicant must show that its original application supports the amended matter. Schering Corp. v. Amgen Inc., 222 F.3d 1347, 55 USPQ2d 1650 (Fed. Cir. 2000). "To establish inherency, the extrinsic evidence 'must make clear that the missing descriptive matter is necessarily present in the thing described in the reference,' and that it would be so recognized by persons of ordinary skill. Inherency, however, may

not be established by probabilities or possibilities." In re Robertson, 169 F.3d 743, 745, 49 USPQ2d 1949, 1950-51 (Fed. Cir. 1999) (citations omitted).

It is respectfully submitted that the original specification was already sufficient to clearly disclose to persons of ordinary skill in the relevant art that nature of the invention and that that the inventors had possession, as of the filing date of the application relied on, of the specific subject matter later claimed by them. Moreover, the Examiner has not met his burden on raising the new matter objection because no evidence or reasons why persons skilled in the art would not recognize in the original disclosure a description of the invention defined by the amended specification and amended claims. It is further submitted that persons of ordinary skill already know and understand that the category of polymerization reactions include emulsion polymerization, solution polymerization and bulk polymerization. Furthermore, it is well known and understood by such persons that the category of emulsion polymerization reactions includes various types, including but not limited to, conventional or "classical" emulsion polymerization and miniemulsion polymerization. See, e.g., Gilbert, R.G., Emulsion Polymerization: A Mechanistic Approach, Academic Press, Chapter 1, pages 12-14 (1995) (copy submitted herewith).

It is further respectfully submitted that persons of ordinary skill in the art would have recognized that the process disclosed in the original specification was clearly conventional type emulsion polymerization because of the required use of a monomer transport aid (such as cyclodextrin, to transport the monomer from the monomer droplets to the aqueous phase where polymerization occurs) and the absence of a co-surfactant. This is in clear contrast to miniemulsion which does not require the use of a monomer transport aid (since polymerization primarily occurs within the monomer droplets and, therefore, the monomer does not need to be transported) and the required presence of a co-surfactant to maintain the integrity of the monomer droplets. See, e.g., Ishikawa et al. (U.S. Patent No. 6,190,767; corresponding to WO 97/07174) and Craun et al. (both describing miniemulsion systems without monomer transport aids, and requiring co-surfactants); see also, Sudol, E. and El-Aasser, M., Miniemulsion

Polymerization, John Wiley & Sons Ltd, Chapter 20, pages 701-704 (1997) (copy submitted herewith). It is noted that amended independent Claim 1, presented hereinabove, now clarifies and recites that the monomer droplets comprise, among other things, a monomer transport aid.

In the foregoing circumstances, it is respectfully submitted that the February 2004 amendments to the specification which lists types of emulsion polymerization suitable for the present invention merely restates that which was already known and understood by persons of ordinary skill in the art based upon the disclosure of the original specification and the general knowledge of such persons. Thus, it is further submitted that the February 2004 amendments to the specification which lists types of emulsion polymerization did not introduce new matter into the present specification and Applicants respectfully request that the Examiner withdraw this objection.

With respect to the additional language added by the February 2004 amendments to Example 5 and the table provided in Example 5, it is respectfully submitted that persons of ordinary skill in the art would have recognized and understood the procedure to be used to test polymer product for the presence of gelled chains therein based upon their own general knowledge and the inclusion in the original specification of the information in the table of Example 5, particularly, the information provided in the column entitled "Notes" wherein the term "(5% in THF")" is specified. Persons of ordinary skill in the art are well-aware of the standard test for the presence of gelled (crosslinked) chains in polymers wherein the polymer is dissolved in a suitable solvent, such as tetrahydrofurane (THF), toluene, or chloroform, and any undissolved solids that are observed constitute gelled (crosslinked) chains. Since this procedure effectively separates gelled chains from non-gelled (uncrosslinked) chains, it is known to be useful in the art for purification of gelled chain polymers, i.e., to remove and wash away any non-gelled chains that may be present in a crosslinked polymer product. See, e.g., Matsumoto, A., et al., *Amphiphilic Polymethacrylates as Crosslinked Polymer Precursors Obtained by Free-Radical Monomethacrylate/Dimethacrylate Copolymerizations*, Journal of Polymer Science: Part A: Polymer Chemistry, Vol.

38, page 4397, John Wiley & Sons, Inc. (2000) (demonstrating purification of polymer by dissolving non-gelled chains using THF, without any detailed discussion); Crompton, T.R., *Analysis of Polymers: An Introduction*, *Chapter 7 Fractionation and molecular weight*, pages 222-223, Pergamon Press (1989) (demonstrating use of chloroform to separate polystyrene polymer into its gel and non-gelled fractions, without any further detailed explanation); and Collins, E.A., et al., *Experiments in Polymer Science*, Experiment 30: Swelling of Network Polymers, pages 481-483, A Wiley-Interscience Publication (1973) (showing test for uncrosslinked polymer chains using toluene as a solvent, without any further explanation) (copies submitted herewith).

It is submitted that the fact that the polymer testing procedures are presented in the foregoing references without any detailed explanation beyond identification of the suitable solvent to be used for the particular polymer involved is indicative of the level of general knowledge held by persons of ordinary skill in the art. Thus, it is further submitted that, in view of the disclosures of the foregoing references, identification of THF in the original specification, as the suitable solvent for testing the polymer produced by the process of the present invention, would have been sufficient to identify the appropriate procedure to teach persons of ordinary skill in art how for confirming successful practice of the process of the present invention.

In the foregoing circumstances, it is respectfully submitted that the February 2004 amendments to the specification which added text to Example 5 and to the table in Example 5 simply amplified and restated descriptive matter already present in the specification, so as to provide a more clear and complete explanation of that which was already known and understood by persons of ordinary skill in the art based upon the disclosure of the original specification and the general knowledge of such persons. Thus, it is further submitted that the February 2004 amendments to the specification which added text to Example 5 did not introduce new matter into the present specification and Applicants respectfully request that the Examiner withdraw this objection.

Claim Rejections Under 35 U.S.C. § 112, second paragraph

On page 4-5 of the final Office Action, the Examiner has rejected Claims 1 and 7-13, under U.S.C. § 112, first paragraph, as being indefinite. This rejection is based on the Examiner's determination that the claim(s) contain subject matter (i.e., "conventional emulsion polymerization") not described in the specification in such a way as to reasonably convey to one skilled in the art that the inventors, at the time of filing, had possession of the claimed invention. Applicants respectfully traverse this rejection because, as explained hereinabove, persons of ordinary skill already understand based on the general knowledge in the art and the original disclosure, that emulsion polymerization includes conventional emulsion and miniemulsion polymerization, among other types, and also that the process described in the specification and examples constitutes conventional polymerization (from the use of a monomer transport aid and the absence of a co-surfactant).

The Board of Patent Appeals and Interferences has acknowledged that "[a]pplicants frequently discover during the course of prosecution that only a part of what they invented and originally claimed is patentable." In re Johnson, 558 F.2d 1008, 1018 (CCPA 1971). This, of course, necessitates that applicants make amendments to the claims during prosecution. The general rule is that a patentee may claim less than he may have the right to claim without showing criticality. See Ex Parte Dresser Ind. Inc., 224 U.S.P.Q. (BNA) 841 (Bd. Pat. App. Interfer. 1983) (citing In re Johnson, 558 F.2d 1008, 1018 (CCPA 1971)).

By the amendments submitted in the February 2004 Amendment, Applicants have simply amended independent Claim 1 to recite and cover less than all of what was originally covered and which was understood to be included by persons of ordinary skill in the art. In other words, persons of ordinary skill in the art already understood, based on the general knowledge in the art and the original specification, that emulsion polymerization includes, among other types, conventional emulsion polymerization and miniemulsion polymerization, and also that Applicants' invention comprises conventional emulsion polymerization, as distinguished from miniemulsion polymerization. Applicants now claim a subset

(conventional emulsion) of the originally disclosed genus of emulsion polymerization reactions suitable for use with the process of the present invention, as permitted under US patent law.

In the foregoing circumstances, withdrawal of the rejection of Claims 1 and 7-13, under U.S.C. § 112, first paragraph, is hereby respectfully requested, because the term conventional emulsion polymerization is not indefinite and was supported by the disclosure provided by the original specification and examples.

Claim Rejections Under 35 U.S.C. §§ 102 and 103

On page 5 of the Office Action, the Examiner has rejected Claims 1 and 8-13, under U.S.C. § 102(b), as being anticipated by Ishikawa et al. (U.S. Patent No. 6,190,767; corresponding to WO 97/07174) for the reasons cited in the previous action. Claims 1 and 8-13 have been rejected, under U.S.C. § 102(e), as being anticipated by Craun et al. (U.S. Patent No. 6,242,531), for reasons cited in the previous action. And finally, on page 6 of the final Office Action, the Examiner has maintained the rejection of Claim 7, under 35 U.S.C. § 103(a), as being obvious and unpatentable over Ishikawa et al. or Craun et al., for reasons cited in the previous action. Applicants respectfully traverse these rejections for the reasons which follow.

The present invention, as recited in amended independent Claim 1, relates generally to a process for preparing an aqueous dispersion of polymeric particles comprising a polymeric composition having non-gelled polymer chains. More particularly, the inventive process involves the step of preparing an aqueous emulsion of hydrophobic monomer droplets and which comprise at least one C_8 to C_{30} alkyl (meth)acrylate monomer, at least one chain branching monomer in an amount not greater than 0.10 weight percent based on the total weight of the C_8 to C_{30} alkyl (meth)acrylate monomer, at least one monomer transport aid, and at least one emulsifier. The process of the present invention, as recited in amended independent Claim 1, also comprises the step of polymerizing, by at least one technique selected from the group consisting of conventional emulsion polymerization, bulk polymerization and solution

<u>polymerization</u>, the C_8 to C_{30} alkyl (meth)acrylate monomer with the chain branching monomer(s) using at least one free radical initiator to form the aqueous dispersion of polymer particles comprising a polymeric composition having non-gelled polymer chains, wherein the polymeric composition has a weight average molecular weight of at least 100,000 g/mol.

It is respectfully submitted that neither of the references cited by the Examiner (i.e., Ishikawa et al. and Craun et al.) either anticipate or make obvious the process of the present invention for the following reasons.

Initially, neither Ishikawa et al. nor Craun et al. teach that the polymerization step may be performed by <u>conventional emulsion polymerization, bulk polymerization or solution polymerization</u>, as recited in amended independent Claim 1 of the present application. Rather, both Ishikawa et al. and Craun et al. teach processes based upon <u>miniemulsion</u> polymerization techniques and both references take great care to distinguish the miniemulsion polymerization processes described therein from conventional or "classical" emulsion polymerization (see, generally, Ishikawa et al. at Columns 5-6; and Craun et al. at Columns. 2-4). Miniemulsion polymerization, on the other hand, is excluded from the present invention as recited in amended independent Claim 1. Applicants hereby incorporate and reiterate the explanations and arguments presented previously on this issue in the February 2004 Amendment.

Furthermore, neither Ishikawa et al. nor Craun et al. teach that the aqueous emulsion of hydrophobic monomer droplets must comprise <u>at least one monomer transport aid</u>. As discussed hereinabove and in the prior February 2004 Amendment, both Ishikawa et al. and Craun et al. clearly and specifically disclose miniemulsion processes in which monomer transport is not an issue and, therefore, no monomer transport aids are required in miniemulsion processes. In this regard, it is respectfully noted that Ishikawa et al. and Craun et al. each explain that in conventional emulsion polymerization, polymerization of the monomers occurs in the aqueous stage of the emulsion and/or in micelles formed by emulsifier (see Ishikawa et al. at Col. 1, lines 48-59; and Craun et al. at Col. 2, lines 55-64). In miniemulsion polymerization processes, such as those

disclosed in these two references, polymerization of the monomers occurs in the monomer droplets because the monomer simply does not migrate into the aqueous phase or into micelles (see Ishikawa et al. at Col. 5, lines 52-54 and at Col. 6, lines 30-31; and Craun et al. at Col. 3, lines 9-10).

Furthermore, the miniemulsion processes disclosed in both Ishikawa et al. and Craun et al. require the use of a co-surfactant, which is not required by the process of the present invention to operate successfully, as recited in amended independent Claim 1.

Based upon the foregoing distinctions, it is respectfully submitted that amended independent Claim 1, as well as dependent Claims 7-13, which depend directly or indirectly therefrom, are patentable over both Ishikawa et al. and Craun et al. Withdrawal of the claim rejections based upon 35 U.S.C. §§ 102 and 103 is hereby requested.

In view of the foregoing amendments and remarks, re-examination of allowance of amended independent Claim 1, as well as dependent Claims 7-13, are respectfully requested.

CONCLUSION

A fee of $420 is believed to be due in connection with the submission of the Amendment portion of this paper, since it is being submitted within two months after the originally set due date for response to the Office Action. This $420 fee is addressed by the accompanying Petition for Extension, which authorizes this $420 to be charged to **Deposit Account No. 18-1850**.

No additional fees are believed to be due in connection with the submission of this Amendment. If, however, any such fees, including petition and extension fees, are due in connection with the submission of this Amendment, the Commissioner is hereby authorized to charge such fees to **Deposit Account No. 18-1850**. In the meantime, please direct all future correspondence relating to the present application to the undersigned attorney.

Respectfully Submitted,

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Date: **September 16, 2004**

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Emulsion Polymerization

A Mechanistic Approach

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Australian National University

Chapters 1-3 written in collaboration with Dr Gregory T Russell

1995

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condition, an advantage of which is that production rates can be optimized by maintaining the system in a state in which the rate of conversion of monomer into polymer is at a maximum (i.e., under conditions such that the gel effect is at its peak; the gel effect is an acceleration in the rate of polymerization often seen at higher conversion, and is discussed in Chapter 4). In continuous processes, pre-prepared latex particles may need to be fed into the reactor so as to replace other particles as they are removed.

A common technique in emulsion copolymerizations is *starved-feed* or *continuous addition*, whereby the polymer is forced to have a fixed composition by feeding in the monomers in the required ratio, while ensuring that the conditions are such that monomer feed is the rate-determining step in particle growth.

1.2.4 Suspension, precipitation, dispersion, miniemulsion, microemulsion and inverse emulsion polymerizations

A variety of different heterogeneous polymerization systems are in use, of which emulsion polymerization is the most common. These are summarized in Table 1.2, and are as follows.

Table 1.2. The different types of heterogeneous polymerization systems.

type	typical particle radius	droplet size	initiator	continuous phase	discrete phase (particles)
emulsion	50–300 nm	≈ 1–$10\ \mu m$	water-soluble	water	initially absent, monomer-swollen polymer particles form
precipitation	50–300 nm	monomer usually water-soluble	water-soluble	water	as in ordinary emulsion polymerization, but monomer does not swell polymer
suspension	$\geq 1\ \mu m$	≈ 1–$10\ \mu m$	oil-soluble	water	monomer + formed polymer in pre-existing droplets
dispersion	$\geq 1\ \mu m$	–	oil-soluble	organic (poor solvent for formed polymer)	initially absent, monomer-swollen polymer particles form
microemulsion	10–30 nm	≈ 10 nm	water-soluble	water	monomer, co-surfactant + formed polymer
inverse emulsion	10^2–10^3 nm	≈ 1–$10\ \mu m$	water- or oil-soluble	oil	monomer, water + formed polymer
miniemulsion	30–100 nm	≈ 30 nm	water-soluble	water	monomer, co-surfactant + formed polymer

An *emulsion* polymerization starts with water, monomer, surfactant and a water-soluble initiator, the monomer being present in large droplets and in the micelles. Polymerization results in the formation of a new particle phase, comprising monomer and

polymer, and stabilized by surfactant. The locus of polymerization is the new particle phase, not the emulsion droplets.

A *precipitation* polymerization [14] is one in which monomer is soluble in the continuous phase (e.g. the water-based polymerization of acrylonitrile, which is completely soluble in water) and where the monomer does not swell its polymer. Thus a latex forms (in the acrylonitrile system, this happens as polymer precipitates out of the water-monomer solution), but since polymer is not swollen by monomer, the locus of polymerization is in the particle–water interface. Precipitation polymerization systems can be understood in terms of models of emulsion polymerization.

A *suspension* polymerization starts with water, monomer, surfactant and an oil-soluble initiator (e.g. benzoyl peroxide or AIBN) rather than a water-soluble initiator. The ingredients are much the same as those for an emulsion polymerization, but the locus of polymerization is in the large monomer droplets, which become the polymer phase. Since the formed polymer is usually insoluble in monomer, this results in a granular product. PVC is commonly manufactured by this means.

A *dispersion* polymerization [15] starts with monomer, an organic-phase initiator, an organic solvent such as heptane in which the forming polymer is insoluble, and either a polymeric stabilizer or a substance (e.g. polyisobutylene-co-isoprene) that will form this on reaction with polymer. The continuous phase comprises solvents (such as *iso*octane for MMA suspension polymerization) in which monomer is soluble but polymer is insoluble. Polymer forms in the continuous phase, and precipitates out into a new particle phase, stabilized by surfactant, wherein polymerization continues: both the continuous and the dispersed phases are organic. A detailed mechanism for this system, based on the same precepts as those in emulsion polymerization, has been given by Paine [16] and the Lehigh group [17,18]. Small particles are formed by aggregation of growing polymer chains precipitating from the continuous phase as these chains exceed a critical chain length. Coalescence of these precursor particles with themselves and with their aggregates results in the formation of colloidally stable (mature) particles, which occurs when sufficient stabilizer covers the particle surfaces.

A *microemulsion* starts with water, monomer, surfactant and (usually) a co-monomer (e.g. hexanol), to which a water-soluble initiator is added. A stable microemulsion is produced (comprising extremely small droplets, larger than micelles but much smaller than ordinary monomer droplets; this microemulsion is usually transparent). A water-soluble initiator is added, and polymer forms inside the microemulsion droplets: the polymerization locus is the pre-existing droplets. The mechanisms in microemulsion polymerization have been discussed by a number of authors [19-24]. The resulting particles are very small and typically contain only a few polymer chains, as distinct from particles formed in an emulsion polymerization, which contain a large number of chains.

An *inverse emulsion* [25] polymerization starts with an organic continuous phase, surfactant, water- or oil-soluble initiator, and a water-soluble monomer such as acrylamide. The droplets comprise water and monomer, and the polymerization locus is usually the pre-existing droplets.

A *miniemulsion* polymerization is intermediate between a microemulsion and an ordinary emulsion polymerization. Ingredients comprise monomer(s), water, surfactant and a co-surfactant such as 1-hexadecanol (cetyl alcohol), dodecanol or hexadecane. The co-surfactant is chosen so that the emulsion droplets which form prior to the commencement of polymerization are very small but not thermodynamically stable. Mechanisms and typical data have been given by a number of authors [26-3. conditions are chosen carefully, all particle formation occurs by entry of a radical into a pre-existing miniemulsion droplet, which is then the locus of polymerization. A

our case

Teaches away from our invention

miniemulsion polymerization can offer some technical advantage over a conventional emulsion polymerization under special circumstances. For example, if the polymerization involves a very water-insoluble ingredient which will therefore transport very slowly through the aqueous phase in a conventional emulsion polymerization, this ingredient can be put directly in the miniemulsion droplets which are the locus of polymerization in a miniemulsion polymerization. Again, under some circumstances, the latex in a miniemulsion polymerization can have a different viscosity and different colloidal stability from that formed with the same monomers in a conventional emulsion polymerization (e.g. [31]).

our transport aid addresses this transport problem

1.3 Advantages and disadvantages of emulsion polymerization

Emulsion polymerizations are in wide commercial use because of their many advantages; however, the process is not without its drawbacks.

1.3.1 Advantages

Some of the reasons for the wide industrial application of emulsion polymerization as a means of producing polymer are as follows.

- The heat generated by the (highly) exothermic free-radical polymerization process can be both readily absorbed (water has a high heat capacity) and dissipated by the aqueous phase, if necessary using reflux condensation. This means that less stringent precautions are required to prevent overheating of reactors.
- The rate of polymerization is usually considerably greater than in an equivalent bulk process, thereby allowing faster throughput for a given capital expenditure.
- In the absence of modifier, the polymer that is formed usually has a considerably higher average molecular weight than that from an equivalent bulk process; as well, it has a different molecular weight distribution.
- The polymer is formed as a latex rather than as the solid or as the viscous solution that would result from the bulk and solution polymerization processes respectively. It can thus be handled much more easily: e.g. a high solids (40–65% by weight) latex can be easily pumped. Formed polymer can be readily obtained by evaporating the water (as occurs when an ordinary latex paint dries on a wall).
- Because the molecular weight is very high in the absence of chain-transfer agents, molecular weight is easily controlled by the addition of chain-transfer agents — this gives additional control of the properties (e.g. mechanical strength) of the formed polymer and of the latex (e.g. minimum film-forming temperature).
- The process itself, and the resulting polymer latex, is water- rather than solvent-based, which reduces both safety and environmental hazards.
- An emulsion polymerization can easily be carried through to relatively high conversion of monomer into polymer; hence any problems with residual monomer are minimized, and monomer consumption is maximized [32].

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1.3.2 Disadvantages

Emulsion polymerization has certain attendant disadvantages, especially the following.

- The system generally contains a large number of additives and these may impair the quality of the final product. For example, it is usually difficult (or expensive) to remove the initiator decomposition products and the surfactant. Hence these are usually present in the polymer product and may therefore be responsible for undesirable product attributes such as unwanted color on molding.
- It may be necessary to separate the polymer from the water, e.g. by coagulation and dewatering, for further processing, which will cause production expenses to be increased.
- Because the polymerization process is heterogeneous and involves a minimum of two phases, mechanisms are extremely complex, and thus hard to understand and hence to control. Indeed, this understanding is the principal objective of the present text.

1.4 A guided tour

The reader of this book will probably have visited a new location and wanted to look around. Often, a Guided Tour is the best way to start. The dedicated tourist wants to explore and experience the sights and culture without a guide, but a guided tour gives the overview that facilitates subsequent individual exploration. That is the objective of this chapter: to describe the mechanisms and outcome of a particular emulsion polymerization, at a molecular level. This mechanistic description will be given without any experimental or theoretical justification, because its objective is to aid comprehension rather than to provide rigor. The remaining chapters provide all the rigor that the purist could desire.


monomer droplets

5 µm
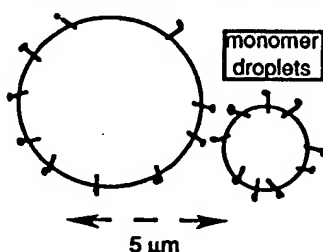
The system for our tour comprises styrene as monomer, water, persulfate as initiator, and surfactant (at a concentration above the cmc). Shear is applied (i.e., the system is stirred), and the monomer and surfactant form an emulsion, where the droplets are polydisperse and of order microns in size (see sketch on left; the ⌐ represents a surfactant molecule).

1.4.1 Particle formation

The persulfate (entirely located in the aqueous phase) now starts to decompose:

$$S_2O_8{}^{2-} \rightarrow 2\,SO_4{}^{-\bullet}$$
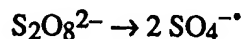
Styrene is very slightly soluble in the aqueous phase, the solubility being 4×10^{-3} mol dm^{-3} at 50°C. The sulfate radicals propagate with the rare monomer units (here denoted M) that they encounter in the aqueous phase to produce oligomeric radicals that are relatively soluble in water:

$$SO_4{}^{-\bullet} + M \rightarrow {}^\bullet MSO_4{}^- \,;\, {}^\bullet MSO_4{}^- + M \rightarrow {}^\bullet M_2SO_4{}^-$$
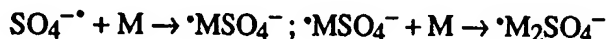
Chapter 20

Miniemulsion Polymerization

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20.1 Definitions

20.1.1 M- - - -emulsions

Oil-in-water dispersions are typically classified as possessing the characteristics of one of three types of emulsions: *macro*emulsions, *mini*emulsions or *micro*emulsions. As the names imply, a major distinction between these three categories is the *size* of the *droplets* (i.e. the discontinuous or dispersed phase) present in these systems. A second major distinction between these three categories is the *stability* of the emulsion. In this context, the "stability" usually refers to the time elapsed prior to noticeable degradation of the emulsion as indicated by the formation of droplets much larger than in the original emulsion, typically noted by the macroscopic separation of the oil phase in creaming experiments.

Figure 20.1 illustrates in a generalized fashion the relationship between the droplet size and the emulsion stability for the three types of emulsions. Macroemulsions are the coarser of the three in that the droplet size is relatively large (1–100 μm) and the stability is limited to minutes. Phase separation is rapid unless the system is well mixed. Droplets continuously collide and coalesce, and are broken by the shear exerted on the system. The droplet size is dependent on the system components (oil, stabilizer, phase ratio) and the mixing characteristics (impeller type and speed). Microemulsions, on the other hand,
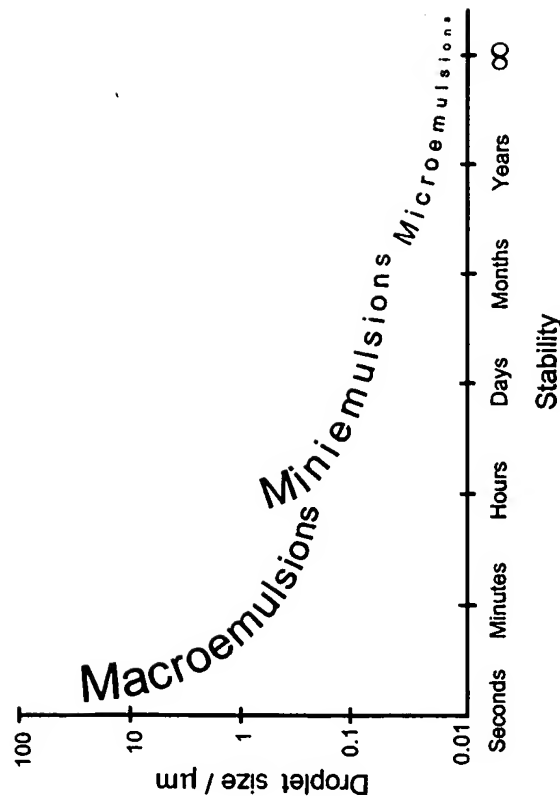
are thermodynamically stable (i.e. indefinitely stable) with droplet sizes varying from 10 to 100 nm. Relatively large quantities of mixed emulsifiers, typically consisting of an ionic surfactant (e.g. sodium dodecyl sulfate, SLS) and a short-chain alcohol (e.g. pentanol), are usually used to prepare these emulsions.
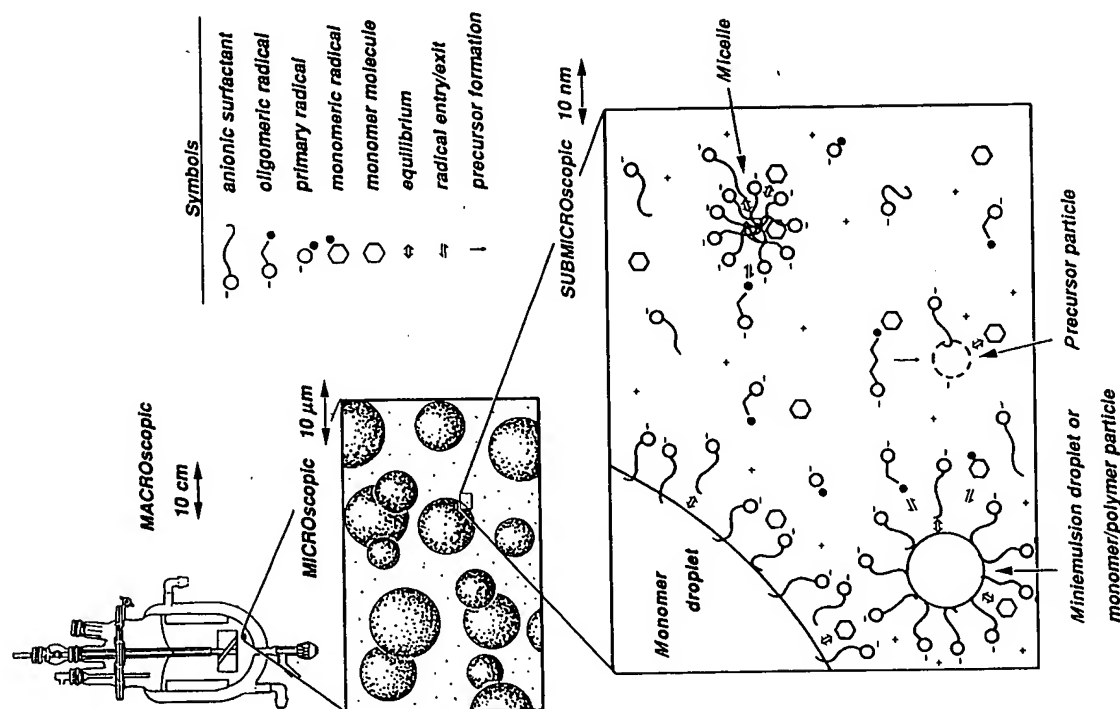
Miniemulsions are considered to lie in between macroemulsions and microemulsions in terms of droplet size and emulsion stability. Droplets generally range in size from 50 to 500 nm and the emulsion can be stable for as little as days and as long as months. The droplets are usually stabilized by the combination of an ionic surfactant (e.g. SLS) and a cosurfactant. The latter usually consists of either a long chain alkane (e.g. hexadecane) or alcohol (e.g. hexadecanol). The function of the cosurfactant can be twofold; it can act in combination with the surfactant to create a barrier to droplet/droplet coalescence by arranging at the oil–water interface and/or it can limit the diffusion of the oil phase from smaller to larger droplets by virtue of its low water solubility which enables a pseudo-equilibrium to be maintained between the droplets of different size and composition. Both mechanisms are considered to be operative for the case of the long-chain alcohols while only the latter can explain the increased stability brought about by use of the alkanes.

Miniemulsions are typically formed by subjecting the oil/water/surfactant/cosurfactant system to a high shear field created by devices such as an ultrasonifier, the Manton Gaulin homogenizer and the Microfluidizer. These rely on mechanical shear and/or cavitation to break the oil phase into submicron size droplets. When monomer is used as the oil phase, free-radical polymerization can subsequently be carried out by addition of an initiator (e.g. potassium persulfate, KPS).

20.1.2 Miniemulsion polymerization

Although it may seem obvious, the definition of miniemulsion polymerization can vary depending on the objectives of the specific research programme. In its narrowest sense, miniemulsion polymerization could be defined as the polymerization of all the monomer droplets present in the initial emulsion, where the final particle size distribution is reflected in the initial droplet size distribution (i.e. there is a one-to-one correspondence between the droplets and particles). It quickly became evident that this definition was too narrow to accommodate most (if not all) of the reactions termed miniemulsion polymerization because there was no such correspondence. Typically, fewer particles were found than the original number of monomer droplets. The definition, therefore, could be taken as the polymerization in miniemulsion droplets where not all the droplets succeed in becoming polymer particles. This definition only allows for nucleation in monomer droplets.

In its broadest sense, miniemulsion polymerization could simply mean the polymerization of a miniemulsion, period. This does not imply any specific

Figure 20.1 Schematic representation of relative stability as a function of droplet size for the three major classes of emulsions

mechanisms and kinetics which could be used to describe the polymerization except those generally found in emulsion polymerization, namely, the initiation, propagation and termination of free radicals in the aqueous and oil (monomer/polymer) phases. In emulsion polymerization, the nucleation of polymer particles is key to the resulting kinetics, particle size distribution and latex properties.

In miniemulsion polymerization, nucleation could take place not only in the monomer droplets but also in micelles (if present) and in the aqueous phase (homogeneous nucleation), as illustrated by the generalized schematic of emulsion polymerization reproduced in Figure 20.2. However, miniemulsions are often prepared with the intent of eliminating nucleation via micellar and aqueous phase routes (i.e. nucleation only in miniemulsion droplets). The former is accomplished by keeping the aqueous phase concentration of the surfactant below its cmc. One way to do this is to choose the initial concentration to be below this value. This, however, is often impractical and thus initial concentrations exceeding the cmc must be used; in these cases, the aqueous phase must be sampled to determine its surfactant concentration to ensure that it is below the cmc (i.e. much of the surfactant is adsorbed at the monomer droplet–water interface).

Ensuring against homogeneous nucleation in miniemulsion polymerization is not as straightforward. Conceptually, nucleation in the aqueous phase should be able to take place at any time. However, in practice it can be reduced by providing free radical "sinks", i.e. droplets and particles. If the lifetime of an oligomeric radical in the aqueous phase can be reduced to below that required for it to grow beyond its limit of water solubility, then homogeneous nucleation can be prevented. The relatively large surface area for radical adsorption provided by the miniemulsion droplets is expected to greatly aid this process. Nonetheless, it is not easy to prove either way whether or not homogeneous nucleation has occurred in a miniemulsion polymerization unless a distinct bimodality in the particle size distribution (or perhaps even the molar mass distribution) is evident. This matter will be revisited several times in this chapter. Suffice it to say, the definition of miniemulsion polymerization can allow for nucleation by any means. However, these kinds of polymerizations may be seen to negate the perceived advantages of polymerization in pre-formed monomer droplets.

20.2 Pros and Cons of Miniemulsion Polymerization

As alluded to earlier, one of the key advantages of miniemulsion polymerizations over conventional emulsion polymerizations was seen to be the direct control over the resulting number of particles which could be achieved by controlling the initial number of monomer droplets. If the latter could be controlled in a reproducible fashion, then the irreproducibilities associated with the creation of latex particles might be eliminated. In conventional emulsion polymerizations, the number of particles is chiefly controlled by the concentrations of surfactant and initiator.

Symbols

- anionic surfactant
- oligomeric radical
- primary radical
- monomeric radical
- monomer molecule
- equilibrium
- radical entry/exit
- precursor formation

MACROscopic 10 cm

MICROscopic 10 μm

SUBMICROscopic 10 nm

Micelle

Monomer droplet

Miniemulsion droplet or monomer/polymer particle

Precursor particle

Figure 20.2 Schematic representation of the early stages of emulsion polymerization illustrating three scales of observation: macroscopic, microscopic and submicroscopic. (Reprinted with permission from E. D. Sudol, E. S. Daniels and M. S. El-Aasser, in Polymer Latexes: Preparation, Characterization, and Applications, E. S. Daniels, E. D. Sudol and M. S. El-Aasser, (eds), ACS Symp. Ser., Vol. 492, 1992, p 1 Copyright © 1992 American Chemical Society)

MINIEMULSION POLYMERIZATION

Table 20.1 Summary of published work on miniemulsion polymerization

Monomer(s)	Surfactant/cosurfactant	Shear	Initiator	T/°C	% Solids	Comments	Reference
Styrene	SLS/CA	Simple mixing	$K_2S_2O_8$	60	25	PSDs reported to be similar to DSDs; droplet diameters < 1 μm	Ugelstad et al., 1973 [1]
Styrene	SHS/CA	Simple mixing	$K_2S_2O_8$	60	25	PSDs bimodal; two nucleation sites-droplets (0.5–1 μm)/ aqueous phase	Ugelstad et al., 1974 [2]
Styrene	SLS/HD	Manton Gaulin	$K_2S_2O_8$ BPO	60	23	PSD's bimodal & unimodal; for KPS cases, latexes were monodisperse	Hansen and Ugelstad, 1979 [3]
Styrene	SLS/DD	Ultra-sonication	$K_2S_2O_8$	50	14–23	Broad PSD's: dual nucleation in droplets (c. 0.1 μm/aqueous phase; low ρ	Chamberlain et al., 1982 [4]
Styrene	SLS/CA	Micro-fluidizer	$K_2S_2O_8$ AMBN	50–70	23	PSD's as broad as DSD's; 0.05 < d < 0.15 μm; slow nucleation of droplets	Choi et al., 1985 [5]
VAc/BA	SHS/HD	Ultra-sonication	$(NH_4)_2S_2O_8$	60	25	Broad PSDs; thermodynamics used to determine monomer partitioning	Delgado et al., 1986 [6]
S/MMA	SLS/HD	Ultra-sonication	$K_2S_2O_8$ AIBN	60	25	Broad PSDs; transport of monomer by collision of droplets with particles	Rodríguez et al., 1989 [7]
BA	SHS/HD	Ultra-sonication	$(NH_4)_2S_2O_8$	75	25	Seeded batch and semi-continuous; droplets nucleated whenever present	Tang et al., 1991 [8]
Styrene	SLS/CA, SLS/HD	Micro-fluidizer	$K_2S_2O_8$	70	20	Broad PSDs; k_s (CA) < k_s (HD); CA acts as chain transfer agent	Tang et al., 1992 [9]

In miniemulsion polymerization, it was initially (if not naïvely) expected that the number of particles would be independent of these variables within certain limits. For most miniemulsion systems, however, this has not been proven to be the case. In particular, the number of particles has been found to be a relatively strong function of the initiator concentration. This is taken as additional evidence for the limited nucleation of the monomer droplets (i.e. only a fraction of the droplets become polymer particles).

If not all of the monomer droplets become polymer particles, this would detract from some of the advantages expected in conducting copolymerizations or encapsulating various materials via the miniemulsion route. In the former case, the limitations of transport of relatively water-insoluble monomers from droplets (non-polymerizing) to growing polymer particles can cause variations in the copolymer composition aside from the differences in the reactivities of the respective monomers. Conceptually, if all monomer droplets were nucleated simultaneously (within several percent conversion of each other), then the copolymer composition in each particle might reflect that in the original droplets. In the case of encapsulation, some inert species such as a dye or pigment would be introduced into the monomer prior to emulsification, followed by polymerization. For all of these to be successfully encapsulated, all of the droplets would have to be nucleated; otherwise unencapsulated material would also be present in the final dispersion.

One can see from these arguments that a key to the successful implementation of miniemulsion polymerization lies in the ability to nucleate all of the droplets created. Recent innovations in miniemulsion polymerization which have the potential for ensuring this are discussed in Section 20.3.2.1(c).

20.3 Miniemulsion Polymerization

Much of what is known about the formation and stabilization of miniemulsions and their subsequent polymerization is derived from studies performed on systems comprising styrene monomer, sodium dodecyl sulfate surfactant, cetyl alcohol (hexadecanol) cosurfactant and potassium persulfate initiator. Variations in the monomer(s), surfactant system, method of preparation, initiator type, temperature of polymerization and final solids contents have all been reported. Many of these studies are summarized by the information given in Table 20.1. This list is not meant to be all inclusive, but serves as a guide to miniemulsion research as reflected in the literature. Based on these works, although primarily those performed with styrene as the monomer, a mechanistic picture of miniemulsion polymerizations has evolved which shows significant differences from the classical picture of emulsion polymerization. The latter is traditionally illustrated using styrene monomer as part of a model system.

20.3.1 Early Work (1973–1983)

Ugelstad et al. [1] reported the first polymerizations of submicron styrene droplets created using a mixed emulsifier system of sodium lauryl (dodecyl) sulfate (SLS) and cetyl alcohol (CA). Although the term "miniemulsion" had not been coined at the time, these polymerizations fit the general definition of miniemulsion polymerization in that droplets smaller than 1 micron were created by simple mixing of the monomer into the aqueous mixed surfactant system followed by polymerization, effected by the addition of potassium persulfate (KPS). The resulting particle size distributions were reported to be qualitatively similar to the initial droplet size distributions, although the former tended to be bimodal in nature. This was taken as an indication that the droplets did indeed become a significant locus of nucleation but not the sole one (i.e. at least two nucleation mechanisms were operative).

Dual nucleation mechanisms were also considered to be operating under given conditions in other styrene miniemulsion systems [2–4]. These include cases where: (1) sodium hexadecyl sulfate was used as the surfactant [2]; (2) hexadecane was used as the cosurfactant and formation of the miniemulsion was accomplished using a Manton Gaulin homogenizer [3]; and (3) dodecanol was used as the cosurfactant with ultrasonification being applied to create the miniemulsions [4]. Following these early studies, miniemulsions have been routinely prepared using some kind of high shear device, in most cases this being either an ultrasonifier or a Microfluidizer [5]. The general conclusion from these works was that the finer the original droplet size (reflected in low aqueous-phase concentrations ([S] <cmc) of the surfactant) the more likely that the droplets would serve as the loci for particle nucleation. That is, the more surface area that is provided for radical absorption, the more likely it is that an oligomeric radical enters (irreversibly) a droplet prior to exceeding its critical chain length which would otherwise result in a precursor particle (by homogeneous nucleation). An additional observation in these early studies was that this entry of radicals into the droplets was a slow process in comparison to entry into polymer particles [3,4]. This observation was made in subsequent work and has become the primary focus of the most recent studies.

20.3.2 Recent work (1984–1995)

Fundamental research on miniemulsion polymerizations has continued throughout the past decade, primarily through reactions carried out using styrene (S) as the sole monomer [5,9,14]. However, other monomers have also been studied in homopolymerizations including butyl acrylate (BA) [8], methyl methacrylate (MMA) [12], vinyl acetate (VAc) [16], and vinyl 2-ethylhexanoate (V2EH) [16]. Miniemulsion copolymerizations have also been the subject of studies on a number of monomer systems including VAc/BA [6], S/MMA [7], and

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Table 20.1 (continued)

Monomer(s)	Surfactant/ cosurfactant	Shear	Initiator	T/°C	% Solids	Comments	Reference
S/2EHA/ MAA	SLS/HD, A-103/HD	Ultra-sonication	$K_2S_2O_8$	75	35–60	Broad PSDs; higher solids content than parallel conventional process	Lopez de Arbina & Asua, 1992 [10]
MMA/BA/ VAc	Aipal CO-436/HD, Brij/HD	Ultra-sonication	$K_2S_2O_8$	80	45–65	Semi-continuous miniemulsion feed; nucleation of droplets	Unzue & Asua, 1993 [11]
MMA	SLS/HD	Ultra-sonication	$K_2S_2O_8$	50	30	Broad PSDs; dual nucleation in droplets and micelles; conductance used as tool	Fontenot and Schork, 1993 [12]
S/2EHA/ MAA	SLS/HD, Aipal CO-436/HD	Ultra-sonication	$K_2S_2O_8$	80	55	Semi-continuous miniemulsion feed; fewer particles and lower latex viscosity compared to conventional latexes	Masa et al. 1993 [13]
styrene	SLS/CA	Micro-fluidizer	$K_2S_2O_8$	70	20	PSD evolution monitored; nucleation period past rate maximum	Miller et al. 1994 [14]
S/PS	SLS/CA	Micro-fluidizer	$K_2S_2O_8$	70	20	Dissolved polymer enhances nucleation efficiency, approaching one ($k_a \downarrow$)	Miller et al. 1994 [15]
VAc/V2EH, VAc, V2EH	40/HD, TREM LF-	Micro-fluidizer	$Na_2S_2O_8$	60	20	R_p (mini) > R_p (conv.); effect of reactive surfactant	Kitzmiller et al., 1994 [16]

VAc = vinyl acetate; BA = n-butyl acrylate; S = styrene; 2EHA = 2 ethylhexylacrylate; MAA = methacrylic acid; MMA = methyl methacrylate; PS = polystyrene; V2EH = vinyl 2-ethylhexanoate; SLS = sodium lauryl sulfate; CA = cetyl alcohol; HD = hexadecane; DD = dodecane; SHS = sodium hexadecyl-sulfate; A-103 = disodium ethoxylated nonyl phenol half ester of sulfosuccinic acid, Cyanamid; Brij 98 = $C_{16}H_{31}$-O-$(C_2H_4O)_{18}$, 35 = $C_{12}H_{25}O$-$(C_2H_4O)_{23}$, ICI; Aipal CO-436 = ammonium salt of sulfated nonylphenoxy poly(ethenoxy) ethanol (4-ethylenoxide), Rhône-Poulenc; BPO = benzoyl peroxide; AMBN = 2, 2'-azobis-(2-methyl butyronitrile); AIBN = 2, 2' azobis(isobutyronitrile); DSD = droplet size distribution; PSD = particle size distribution; ρ = radical entry rate; d = diameter; k_a = radical absorption rate coefficient, R_p = rate of polymerization.

VAc/V2EH [16]. Several studies have also included terpolymerizations: S/2-ethylhexylacrylate (2EHA)/methacrylic acid (MAA) [10,13] and MMA/BA/VAc [11]. These systems and the major findings resulting from their study will be reviewed here.

20.3.2.1 Homopolymerizations
20.3.2.1(a) Styrene

Three separate miniemulsion polymerization studies have been carried out at 70°C using styrene monomer (20–23 wt%), sodium lauryl sulfate (10 mmol dm⁻³ based on the aqueous phase), cetyl alcohol cosurfactant (30 mmol dm⁻³ based on the aqueous phase), and potassium persulfate initiator (variable concentration). Each study has successively added to the knowledge and understanding of the mechanism of miniemulsion polymerization.

Choi et al. [5] used dilatometry to monitor the kinetics of styrene miniemulsion polymerizations employing not only varying KPS concentrations but, in addition, the oil-soluble initiator 2,2'-azobis(2-methyl butyronitrile) (AMBN). The latter was initially thought to provide an increased probability of nucleating all monomer droplets considering that the main locus of initiator decomposition and subsequent chain growth would be in the monomer droplets. This, however, did not prove to be the case.

Using KPS, the rate of polymerization and the number of particles were found to increase with the 0.33 and 0.37 powers respectively, of the initial initiator concentration. These values are not far from the 0.4 power predicted by Smith and Ewart for conventional emulsion polymerization (see Section 4.9) and are within the range reported experimentally. Similar values were more recently reported by Miller et al. (namely, $R_p \propto [I]^{0.36}$, $N_p \propto [I]^{0.31}$) [14]. However, significant differences exist between these two efforts. The resulting particle

sizes (d_n, number-average diameter) and per cent standard deviations for various miniemulsion polymerizations are reported in Table 20.2. It is seen that significantly smaller particles were reported by Choi et al. as compared to those of Miller et al. The source of these differences is unclear. Significant differences would not be expected based on differences in the formulations (23% vs 20% solids). However, the preparative procedure did vary somewhat and could possibly account for differences in the particle sizes. Choi et al. prepared the miniemulsions by: (1) mixing the SLS, CA and water at 65°C (above the melting point of CA) for 1 h; (2) styrene monomer was added and stirred at 65°C for 30 min; and (3) the emulsion was passed through a Microfluidizer (A10 orifice) 10 times. The subsequent polymerizations were carried out at 70°C in a 25 cm³ dilatometer after first degassing the mixture. Miller et al. used a modified form of the above procedure: (1) the SLS, CA and water were mixed at 70°C for 2 h and then cooled to room temperature; (2) this mixture (referred to as the gel phase) was sonified; (3) the styrene was added, mixed for 10 min and sonified; and (4) this emulsion was subjected to 10 passes through a Microfluidizer as above.

Some of the differences between the work of Choi et al. and Miller et al. could be explained by the work of Tang et al. [9] who performed a comparative study on some of the preparation variables in the miniemulsion polymerization of styrene. In one case, the temperature at which the miniemulsion was formed (by passing through a Microfluidizer) was varied (25 and 65°C). The results showed that a smaller particle size resulted for the miniemulsion prepared at the elevated temperature ($d_n(25°C) = 168$ nm; $d_n(65°C) = 147$ nm). These results, however, cannot be compared directly since the latter were conducted using 5 mmol dm⁻³ SLS/15 mmol dm⁻³ CA while the others employed twice these amounts. Nonetheless, these results may help to explain differences noted in the two studies and also point out the difficulty in comparing results obtained by different researchers, even if the work is performed in the same laboratory.

20.3.2.1(b) Kinetics and mechanisms

The recent work of Miller et al. [14,15,17] will be used here to describe the kinetics and mechanisms of the miniemulsion polymerization of styrene. This work not only contains the most detailed kinetics obtained thus far (via calorimetry), but also includes the evolution of the particle size and its distribution (via TEM) with conversion. The conversion versus time (x–t) behaviour for miniemulsion polymerizations carried out with varying KPS concentrations are given in Figure 20.3(a). At first glance, the curves do not appear to be significantly different from what one would expect for conventional emulsion polymerizations, i.e. an S-shaped curve with an additional increase in the rate due to the autoacceleration brought about by the gel effect. These curves could even be interpreted as having a constant rate period as expected in the Interval II of the Smith–Ewart classical description of emulsion polymerization [18]. However, these x–t curves were obtained by integration of the rate of polymerization, R_p,
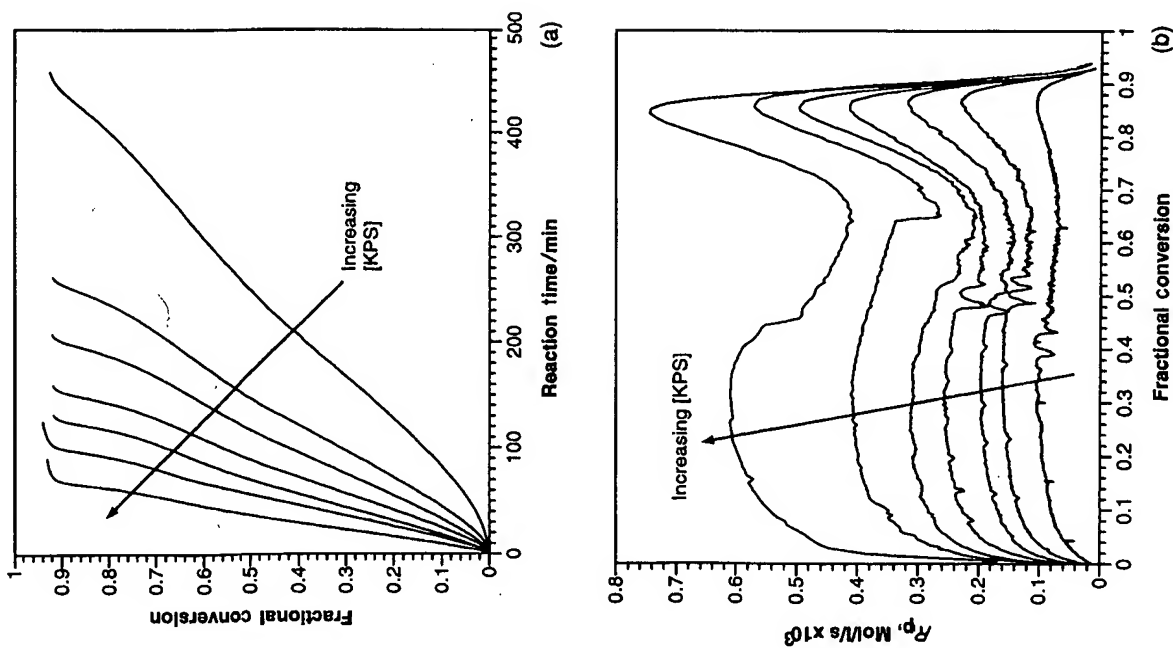
Table 20.2 Particle size as a function of initiator concentration for the miniemulsion polymerization of styrene at 70°C

[KPS]/mmol dm⁻³	Choi et al. [5]		Miller et al. [14]		Miller et al. [15] w/ 1% PS polymer	
	d_n/nm	σ/%	d_n/nm	σ/%	d_n/nm	σ/%
0.133	132.0	10.7	178.3	23.3	—	—
0.333	123.2	10.6	171.3	14.0	67.3	44.9
0.665	110.8	10.9	156.0	14.6	73.6	33.8
1.330	101.8	10.7	151.2	13.5	76.1	29.7
2.660	90.6	11.6	142.3	12.7	71.4	28.3
5.320	—	—	128.5	16.4	75.5	20.8
14.00	—	—	116.3	12.1	—	—
1.33ᵃ	—	—	105.2	11.8	—	—
	$N_p \propto [I]^{0.37}$		$N_p \propto [I]^{0.31}$		$N_p \propto [I]^{0}$	
	$R_p \propto [I]^{0.33}$		$R_p \propto [I]^{0.36}$			

ᵃConventional emulsion polymerization.

data shown in Figure 20.3(b) which were derived directly from the heat of the reaction (using a Mettler RC1). These R_p versus conversion curves have been described by dividing them into four regions (analogous to Intervals *I*, *II* and *III*) based on whether the rate is increasing or decreasing. The initial increase in the rate is rapid with about 90% of it being achieved by 10% conversion; the subsequent increase to a maximum slows up to somewhere between 30 and 40% conversion where the rate begins to decrease. Mechanistically, this behaviour would normally be interpreted to mean that particle nucleation takes place in the miniemulsion droplets up to this maximum and then ceases, the declining rate being attributed to a decreasing concentration of monomer in the polymer particles. This, however, has not proven to be completely correct. Although the monomer concentration in the particles does decrease after the maximum, it actually decreases from the beginning of the polymerization as a consequence of the presence of the cosurfactant in the particles and droplets. This has been shown by thermodynamic analysis of the system [17]. Particle size analysis (TEM) of samples taken throughout the polymerizations has shown that particle nucleation ends between 40 and 60% conversion, beyond the rate maximum. This is considered to be possible because the presence of monomer droplets can persist until late in the polymerization, this also being explained by the presence of the cosurfactant which stabilizes them against diffusive degradation (a pseudo-equilibrium).

The mechanism of disappearance of miniemulsion droplets other than by becoming polymer particles is still not resolved. Although initially it was expected that all droplets could be successfully entered by a free radical thereby becoming polymer particles, only a relatively small fraction (≤20%) succeed in this. Collision between droplets and existing particles, and diffusion are the two mechanisms often cited as possibilities to explain this disappearance, although the former explanation seems favoured. This will be seen later in the S/MMA copolymerization studies (Section 20.3.2.2(b)) [7].

Why do so few miniemulsion monomer droplets succeed in becoming polymer particles? This is an important question in that it has implications from a mechanistic as well as an application point of view. The current thinking is that the radical entry rate coefficient for droplets (k_a^d) is substantially lower that for monomer-swollen polymer particles (k_a^p). This leads to an unfavourable competition between droplets and particles as more particles are produced. This idea is indeed supported by the experimental results and mathematical modelling of miniemulsion polymerization [17]. However, the mechanistic reasons for this are not as clear. Several ideas have been put forth to help explain this phenomenon. The first is that a barrier to radical entry into droplets exists because of the formation of an interfacial complex of the surfactant/cosurfactant at the surface of the monomer droplets. This has been demonstrated for the SLS/CA system [19,20], but would not be the case for the SLS/HD system. Indeed, it has been found that use of the latter does result in much faster initial polymerization kinetics [9],

Figure 20.3 Conversion (a) and rate of polymerization (b) versus time for styrene miniemulsion polymerizations carried out at 70 °C using 10 mmol dm⁻³ SLS/30 mmol dm⁻³ CA and initiated using increasing amounts of KPS (0.13, 0.33, 0.67, 1.33, 2.66, 5.32, and 14 mmol dm⁻³). (Reprinted from ref. 14. Copyright © 1995 John Wiley & Sons, Inc.)

Figure 20.4 . Conversion (a) and rate of polymerization (b) versus time for a styrene conventional emulsion polymerization and styrene miniemulsion polymerizations carried out at 70°C using 10 mmol dm⁻³ SLS/30 mmol dm⁻³ CA and 0, 0.05, 0.5, 1, and 2% polystyrene in styrene solutions, as indicated, with $[KPS] = 1.33$ mmol dm⁻³. (Reprinted from ref. 15(2). Copyright © 1995 American Chemical Society.)

but does not lead to a substantially increased fraction of droplets nucleated. This would indicate that the interfacial barrier does not limit the number of droplets nucleated. Therefore, some other differences must account for the increased radical capture efficiency of particles over droplets. Obviously, the effect of the presence of the polymer must be considered as a candidate for explaining this phenomenon. To this end, the incorporation of polymer into miniemulsion droplets prior to reaction was investigated as an avenue for developing a greater understanding of miniemulsion polymerization.

20.3.2.1(c) Styrene polystyrene miniemulsions

The emulsification of polymer/solvent mixtures in water using mixed emulsifiers and a high shear device is commonly used to prepare artificial latexes. However, replacing the solvent with monomer, followed by emulsification and polymerization, has not been the subject of much published research. In this case, polystyrene in styrene solutions (≤2 wt%) were used to prepare miniemulsions for subsequent polymerization in an investigation paralleling the prior work [15]. The goal was to determine whether or not the presence of polymer in the droplets affected the radical absorption rate or, in other words, whether monomer-swollen polymer particles did indeed have a larger k_a than miniemulsion droplets.

Polymerizations were carried out using miniemulsions prepared with 0.05–2.0 wt% polystyrene in styrene and using SLS/CA (10 mmol dm⁻³/30 mmol dm⁻³) as the stabilization system. The x–t as well as the R_p–t curves are shown in Figure 20.4a and b, respectively. It is obvious from these results that the presence of polymer in the miniemulsion "droplets" had a profound effect on the reaction kinetics, increasing the polymerization rate substantially above that for the ordinary miniemulsion prepared without polymer and even above a parallel conventional emulsion polymerization for all but the lowest amount of added polymer. These results, coupled with particle size analysis (Table 20.2), indicate that, as was speculated, the presence of polymer does indeed influence the radical capture rate, increasing it substantially over droplets containing no polymer. In addition, these results also showed that it is possible to nucleate 100% of the "droplets" provided that the polymer and initiator concentrations exceed certain levels (e.g. 1 wt% polystyrene and >5 mmol dm⁻³ KPS). Below these amounts, the PSDs were found to be bimodal with the smaller particle size peak resulting from droplets never entered by a radical (i.e. made up of only the polymer initially added to the monomer). This itself is an important finding for it may allow for direct control over particle size and copolymer composition for relatively water-insoluble monomers, the initial advantages put forth for miniemulsion polymerization.

The question remains as to the cause of the increased radical entry rate when polymer is present in the droplets. Two possibilities have been suggested which are related to the surface and bulk properties of the droplets respectively. The former explanation contends that the polymer disrupts the packing of the SLS/CA
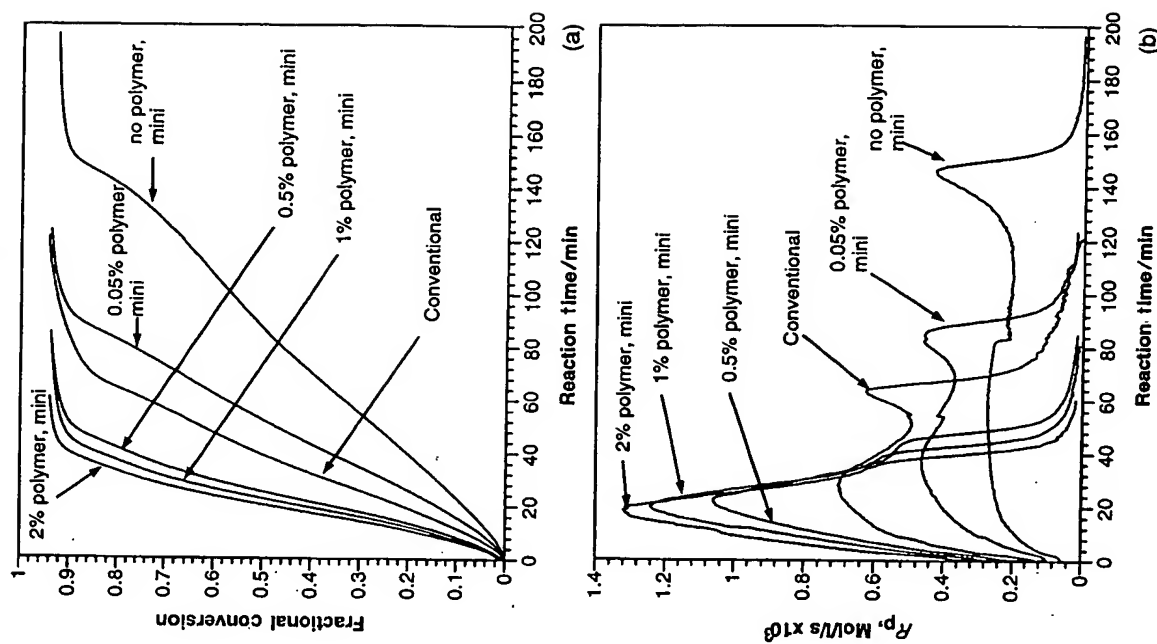
at the droplet–water interface, thereby weakening or eliminating the barrier to radical entry. This is partially supported by results obtained for the polymerization of miniemulsions prepared using hexadecane as the cosurfactant where a much higher initial polymerization rate has been observed and where no such interfacial barrier is considered possible. However, even for these miniemulsions prepared with hexadecane, their polymerization does not result in all droplets being nucleated.

The second explanation for the increased entry rate with polymer present in the droplets is that the polymer modifies the bulk properties (or near-surface bulk properties) of the droplets which favours radical capture. The successful capture of a radical by a particle or droplet is considered to occur only after a relatively large number of encounters which are not successful. The nature of these encounters is the subject of debate and speculation. It is generally accepted that sulfate radical-anions do not readily enter a particle but instead must add a number of monomer units to render them surface active. The fate of such a radical which encounters a particle can be adsorption/absorption (entry), or adsorption/desorption or absorption/exit, the former being a surface phenomenon and the latter being more a "bulk" phenomenon. The reality of these latter events may be merely a combination of the two where the hydrophobic radical-end penetrates the particle surface into the monomer/polymer environment while the terminal sulfate ion remains in the aqueous environment. In any case, the nature of the monomer/polymer phase may increase the ability of the radical to remain in this phase long enough to add another monomer unit which would vastly reduce its ability to exit this phase. The increased viscosity in this region brought about by the presence of polymer may sufficiently reduce the diffusivity of the radical end to increase the probability of adding a monomer unit prior to exit, thus effectively increasing k_a. Future work in this area will need to focus on conducting experiments to clarify this phenomenon.

20.3.2.1(d) Butyl acrylate

Tang et al. [8] utilized n-butyl acrylate (BA) miniemulsions prepared with sodium hexadecyl sulfate/hexadecane in batch and semi-batch reactions where the miniemulsion (prepared by ultrasonification) was fed to a reactor containing a poly(BA) seed latex. In all cases, new particles were generated as a result of nucleation in the monomer droplets. These numbers increased with decreasing initial seed concentration in the reactor illustrating the competition between the seed and the droplets for free radicals. Broad PSDs were produced relative to parallel experiments where neat monomer was fed to the reactor and only relatively small quantities of new particles were generated. For example, the percentage increase in the number of new particles relative to the seed particles increased from 8 to 400% when the polymerization conditions were changed from one in which monomer was added neat to the seed (monomer : polymer ratio, M/P = 9/1) in a batch reaction to the case where a miniemulsion was "fast-fed"

to the reactor. For the latter experiment, the particle size spanned the range from 50 to 450 nm (d_v(volume average diameter) = 212 nm, σ = 53%), whereas the original seed had d_v = 160 nm and σ = 7%. The potential for controlling the PSD of a latex is notable based on these findings.

20.3.2.1(e) Methyl methacrylate

In experiments which roughly parallel the styrene miniemulsion work, Fontenot and Schork have studied the miniemulsion polymerization of methyl methacrylate (MMA) at 50°C using SLS as surfactant, HD as cosurfactant and KPS initiator [12]. These concentrations were varied along with the amount of shear (via sonification time) to establish conditions under which the particle nucleation mechanism varied from primarily micellar through primarily droplet. As might be expected from the prior work with styrene, smaller droplets ensured that the latter mechanism was operative. Relatively low surfactant levels (10–20 mmol dm^{-3} SLS), high cosurfactant levels (10 g HD/220 g MMA), long sonification times (c. 10 min), and low hold times (i.e. prior to initiator addition; <10 min) lead to conditions in which the droplets were small (on the order of 100 nm) and nucleation took place predominantly in these droplets.

Parallel conventional (macroemulsion) polymerizations were run to aid in identifying nucleation mechanisms and conditions in which the rate of polymerization of comparable miniemulsions exceeded that of the conventional emulsion polymerizations. The highest polymerization rates for the miniemulsions were found to be greater than the latter, despite producing larger particles. This somewhat unusual finding was attributed to high monomer concentrations and average number of radicals per particle ($\bar{n}$) in the particles created in the miniemulsion system. MMA polymerizations are typically characterized by a strong autoacceleration due to the gel effect when compared to those of styrene which can lead to Smith–Ewart Case 3 kinetics ($\bar{n} \gg 1$) in many cases.

20.3.2.1(f) Vinyl acetate and vinyl 2-ethylhexanoate

Two monomers with widely differing water solubilities are being compared in miniemulsion and conventional emulsion polymerizations employing a reactive surfactant and its non-reactive counterpart, as part of a study of the copolymerization of these monomers (see Section 20.3.2.2(d)) [16]. Vinyl acetate (VAc) has a water solubility of 2 wt%, which may be compared to that of vinyl 2-ethylhexanoate (V2EH) which is 0.01 wt% (as a reference, the value for styrene is 0.03 wt%). The low value for V2EH was expected to lead to polymerization kinetics reflecting some diffusion limitations of the monomer. In addition, the reactive surfactant sodium dodecyl allyl sulfosuccinate (TREM LF-40) was previously found to copolymerize with VAc at the surface of the growing polymer particles, thereby binding the stabilizer to the particles [21]. This can be a significant advantage over conventional emulsifiers which can only adsorb on the surface of the particles.

20.3.2.2(a) VAc/BA

As a comonomer, VAc is popular because it contributes to certain application properties and is relatively inexpensive. It has found many uses in coatings and adhesives, so much so that it is typically paired with BA as a model system in copolymerization studies. As such, this was the first comonomer pair to be investigated in miniemulsion copolymerizations.

Batch miniemulsion polymerizations of VAc/BA were investigated using 50/50 and 25/75 molar ratios of the two monomers, SHS/HD as the surfactant/cosurfactant system and ammonium persulfate as initiator [6]. The polymerizations were conducted at 60 °C with 25% solids formulations. The miniemulsion droplets were created using ultrasonification. The polymerizations were characterized by their reaction kinetics, copolymer compositions and properties, and final particle size distributions. Parallel conventional emulsion polymerizations (i.e. no cosurfactant, no high shear) were conducted for comparison.

As found in the styrene homopolymerization studies conducted at surfactant concentrations above the cmc, the conventional emulsion polymerizations produced smaller particles and higher polymerization rates than the comparable miniemulsions. The strong dependence of the number of particles on the initiator concentration for the miniemulsion polymerization ($N_p \propto [I]^{0.8}$) indicated that not all of the monomer droplets were nucleated in this system as was the case for all other systems except that containing pre-dissolved polymer. The reason given for this behaviour was again the relatively poor radical absorption efficiency of the monomer droplets. In contrast, however, there was no dependency of the particle number on the initiator concentration for the conventional emulsion copolymerization.

Copolymer rich in BA was produced early in the polymerizations which was followed essentially by homopolymerization of the VAc, producing distinct shapes of the rate and conversion curves reflecting this phenomenon. This was attributed to the disparate values of the reactivity ratios of these monomers ($r_{VAc} = 0.04$, $r_{BA} = 5.5$). Small but significant differences in the development of the copolymer composition were found where the miniemulsion polymerization resulted in a lower VAc content in the copolymer up to a high conversion (70%) as compared to a parallel conventional emulsion polymerization. Thermodynamic treatment of the partitioning of the components in these systems, coupled with a kinetic model, was used to successfully explain these differences. The HD cosurfactant was the key component (by its presence or absence) affecting the monomer distribution between the phases, thereby affecting the copolymerization in the polymer particles. The polymer properties (T_g's and solvent solubilities) were also shown to be affected by the differing polymerizations.

An investigation paralleling the preceding work was conducted on the VAc/methyl acrylate system [22]. For a 50/50 molar ratio with Aerosol MA (sodium dihexyl sulfosuccinate)/HD as the surfactant system, similar results were found as above; the number of particles was proportional to $[I]^{0.63}$

Significant differences have been seen in the kinetics obtained for the miniemulsion and conventional emulsion polymerizations of VAc and V2EH. Both miniemulsion polymerizations were initially faster than their conventional counterparts. This was attributed to a combination of the size of the locus of polymerization (nucleated/growing particles) and the effect of the TREM LF-40. The latter was previously determined to reduce the rate of polymerization of VAc by reacting with the monomer by either chain transfer (the dominant effect) or copolymerization. And because the reactions were primarily at the surface of the latex particles, the effect was enhanced for smaller particles, thus causing the rate of polymerization to decrease with decreasing particle size or increasing particle number which is the opposite of the effect normally seen in emulsion polymerization. Indeed, the final particle sizes from the conventional process (d_n(VAc) = 89 nm, d_n(V2EH) = 101 nm) were smaller than their miniemulsion counterparts (d_n(VAc) = 106 nm, d_n(V2EH) = 168 nm).

In addition, the low water solubility of the V2EH is considered to be partially responsible for the unusual shape of the conventional emulsion polymerization rate curves where a long steady rise to a rate maximum at high conversion (~60%) is characteristic of this and other conventional formulations (i.e. with and without the reactive surfactant). Although the precise kinetic mechanism describing this behaviour has yet to be understood, the diffusion limitation of the monomer through the aqueous phase is considered likely to play a role in determining the rate of polymerization. The reactive surfactant does play a role in slowing the polymerization as with VAc, but only changes the shape of the curve to a small degree (i.e. lower initial rate of reaction compared to systems with the conventional surfactants, SLS and hydrogenated TREM LF-40). These results indicate that a distinct advantage may be gained by employing miniemulsions in the polymerization of relatively water-insoluble monomers. This point is considered further in the following section.

20.3.2.2 Miniemulsion copolymerization

The vast majority of latexes are made with multiple monomers as a means of obtaining the variety of properties that are useful in industrial applications. As mentioned earlier, miniemulsion polymerizations have the added potential advantages of some increased control over the copolymer composition and the copolymerization of monomers of low water-solubility. The preparation of a number of copolymer systems has been and continues to be investigated via this route, as listed in Table 20.1. Many of these investigations have been conducted in a manner similar to the homopolymerization studies, but with the added variable of the monomer ratio and the determination of the copolymer composition as a function of time or conversion. Additionally, the feasibility of conducting miniemulsion polymerizations using a semi-continuous feed and at high solids have also been examined.

for the miniemulsion polymerizations and $[I]^0$ for the conventional emulsion polymerizations over the same range of initiator concentrations. The mechanisms of the polymerization of these two systems were considered to be substantially the same.

20.3.2.2(b) S/MMA

The mechanism by which monomer is transported between miniemulsion droplets and from these to polymer particles was the focus of a study using styrene and methyl methacrylate as comonomers [7]. The SLS/HD surfactant/cosurfactant system was used in this work. Several approaches were applied in an attempt to determine the diffusive mass-transfer coefficients of the monomers as well as the contribution of monomer droplet/polymer particle collision to the monomer transport process. Mass transfer was shown not to be a limitation in miniemulsion polymerization (i.e. equilibrium was satisfied under normal conditions). However, the thermodynamic model developed previously [6] predicted the continued existence of monomer droplets until the end of a miniemulsion polymerization provided that not all droplets were nucleated. Experimentally though, nucleation has been shown to end well before complete conversion which implies another route for monomer droplet disappearance, namely, collision.

Seeded polymerizations were conducted in which S/MMA miniemulsions were added to a copolymer seed (S/MMA 50/50 wt ratio) previously prepared by miniemulsion polymerization using an oil-soluble initiator (AIBN). The amount of HD and the addition of a water-insoluble inhibitor (2,5 di-tert-butyl hydroquinone) to the monomer prior to emulsification were variables, and in one case the agitation rate was reduced. Polymerizations were conducted at 60°C with the radicals being provided either by the residual initiator remaining with the seed or by addition of KPS. It was inferred from the resulting polymerization kinetics and particle size distributions that the inhibitor originally in the miniemulsion droplets was transported to the seed particles through collision of the two species (i.e. transport by molecular diffusion was precluded). The rate of polymerization was lower not only with the addition of the inhibitor (no new particles formed) but also at the higher agitation rate (increased collision frequency between droplets and particles). Under the given conditions, the relative amount of inhibitor transported by collision (vs diffusion) varied from 33 to 80%. This information was subsequently used to successfully model the polymerizations described above [23].

20.3.2.2(c) VAc/V2EH

The homopolymerizations of these two monomers were studied previously (see Section 20.3.2.1(f)) with the intent of using them in combination in batch miniemulsion and conventional emulsion copolymerizations. Formulations and polymerization conditions parallel the preceding work with the main variable

being the molar ratio of the VAc/V2EH monomers (75/25, 50/50, 25/75). The miniemulsion polymerizations (60°C) produced particles of increasing size with increasing V2EH content (d_n = 125, 139, 145 nm, respectively) while the polymerization rate profiles were only slightly affected, resembling their V2EH homopolymerization counterpart (i.e. quick rise to a plateau followed by a decrease). Parallel conventional emulsion polymerizations, in contrast, produced smaller particles but no trend was noted (d_n = 81, 63, 80 nm, respectively) while the rates varied proportionally to the monomer ratio with the total reaction time increasing with V2EH content (i.e. lying between the respective homopolymerizations). These differences were again attributed to the initial size and composition of the locus of polymerization (i.e. particles nucleated from droplets containing the cosurfactant being much larger than those nucleated in conventional emulsion polymerizations) which determine the retarding effect of the reactive surfactant and the distribution of the monomers between the droplets and particles. Although in this case, an advantage of miniemulsion copolymerization over conventional emulsion copolymerization may be seen in terms of an increased rate of polymerization, this work has yet to show whether or not miniemulsion polymerization provides some advantage in terms of improved control over the copolymer composition which was the primary reason for this study.

20.3.2.3 High solids terpolymerizations

In order to gain more industrial relevance, the feasibility of preparing high solids latexes via polymerization of miniemulsions was investigated in terpolymerizations of styrene/2-ethylhexylacrylate/methacrylic acid (45/45/10 mole ratio). Variables included the surfactant (type and concentration), initiator (concentration), solids content and addition mode (batch [10] and semi-continuous [13]).

In batch experiments, the solids were varied from 35 to 75% [10]. The primary surfactant was Aerosol A103 (disodium ethoxylated nonyl phenol half ester of sulfosuccinic acid) with HD as the cosurfactant. These were used in concentrations of 1 and 4 wt% on monomer, respectively. Two KPS concentrations, 1 and 2 wt% on water, were tried. The miniemulsions were produced by ultrasonification. Parallel conventional emulsion polymerizations were conducted for comparison to the miniemulsion polymerizations (75°C). Coagulum-free latexes resulted from miniemulsion polymerizations up to 60% solids, while only 50% solids could be achieved for the conventional process. These differences were attributed to the resulting particle size distributions where the miniemulsion polymerizations produced latexes with larger particles, broader distributions and lower viscosities than their conventional counterparts. As in other studies, this difference in PSDs was explained by differing nucleation mechanisms. However, as in other studies, it was not possible to determine whether the nucleation in the miniemulsion systems was predominantly by radical entry into droplets.

Semi-continuous polymerizations also were performed at 80 °C and 55% final solids by feeding the termonomer miniemulsion to a reactor after initially creating a seed by batch polymerization of an initial miniemulsion charge [13]. In this case, the polymerization kinetics revealed a slower reaction for the miniemulsion feed in comparison to a reference conventional semi-continuous process. This would be expected based on previous studies showing miniemulsions producing larger particles and broader distributions than their conventional counterparts. Particle nucleation also appeared to take place to some extent throughout the miniemulsion polymerizations, as was seen in the studies with butyl acrylate [8].

A second terpolymerization system was investigated for the purpose of preparing high solids latexes via semi-continuous miniemulsion polymerization at 80°C: MMA/BA/VAc (35/50/15 mole ratio) [11]. This system actually contained a fourth monomer, acrylic acid, added as 1 wt% based on monomer. In addition, the use of ionic/nonionic mixed surfactant systems was investigated (Alipal CO 436/Brij 35 primarily) along with HD as the cosurfactant. A host of process conditions were varied to determine their effects on the polymerization kinetics (conversion and $\overline{n}$), evolution of particle size, particle number and terpolymer composition, and coagulum formation. As in the preceding cases, continuous nucleation was always found when a miniemulsion was fed to the reactor, a consequence of the nucleation of the stable miniemulsion droplets. Drift in the copolymer composition could be minimized by operating at high instantaneous conversions. This, however, is the same strategy that is applied in conventional emulsion copolymerizations (see Section 7.4.4). No comparisons of the evolution of the copolymer composition between miniemulsion and parallel conventional emulsion polymerizations were made in this study. Conditions were found in which a 65% solids content latex could be made by semi-continuous miniemulsion polymerization in which a 55% solids initial charge in the reactor and a feed of 66.1% solids (including Alipal CO 436 (2 wt%) and Brij 98 (2 wt%)) were utilized. This work suggests that miniemulsions can be applied to the preparation of industrially relevant latexes.

20.4 Prospects

The preceding investigations have taken two approaches: (1) to gain a fundamental understanding of the mechanisms of miniemulsion polymerizations; and (2) to challenge the technique by applying it in areas where it might compete with conventional emulsion polymerization. Significant advances have been made in both of these over the past few years, and both areas continue to be pursued in current studies.

The ability to nucleate all the monomer droplets without having to rely on monomer transport from non-nucleated droplets to growing particles may now be possible with inclusion of a small amount of polymer in the droplets. This technique has the potential for achieving the original goals of applying miniemulsions

in polymerizations, that is, direct control over the particle size and composition. However, it is not known how the incorporation of polymer acts to control the nucleation process. Research is ongoing in this area including both experimental and theoretical (kinetic and thermodynamic modelling) components focusing on the radical entry mechanism and distribution of components between the phases. This work is being pursued in both homopolymerization and copolymerization systems.

The high solids content studies using monomer miniemulsions in batch and semi-continuous processes was shown to lead to higher solids content, low coagulum latexes compared to those prepared in parallel polymerizations in which the monomer is not pre-emulsified. However, the extent of polymerization in monomer droplets is not known, being inferred from the experimental conditions and results. Nonetheless, some advantage has been demonstrated in these investigations for applying miniemulsion technology to the preparation of high solids latexes. This is expected to become an increasingly important area of investigation if miniemulsion polymerization is to take its place beside conventional emulsion polymerization as a process for preparing latexes useful in industrial applications.

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Amphiphilic Polymethacrylates as Crosslinked Polymer Precursors Obtained by Free-Radical Monomethacrylate/Dimethacrylate Copolymerizations

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ABSTRACT: As an extension of our work on the elucidation of the mechanism and control of 3-dimensional network formation in the free-radical crosslinking polymerization and copolymerization of multivinyl compounds with the aim to molecularly design vinyl-type network polymers, novel amphiphilic polymers were prepared as crosslinked polymer precursors. Thus, benzyl methacrylate, a nonpolar monomer, was copolymerized radically with 5 mol % of triicosaethylene glycol dimethacrylate $[CH_2=C(CH_3)CO(OCH_2CH_2)_{23}OCOC(CH_3)=CH_2]$, a polar monomer, in the presence of lauryl mercaptan as a chain transfer agent. The resulting prepolymers (i.e., vinyl-type network-polymer precursors or amphiphilic polymers) were characterized mainly by viscometry using t-butylbenzene (t-BB) and a t-BB/MeOH (80/20) mixture as solvents. The viscosities in the t-BB/MeOH (80/20) mixture were quite high compared with those in t-BB, and completely reversed concentration dependencies were observed in the solvents. These are discussed by considering the difference in conformation and the shrinkage of polar, flexible polyoxyethylene units or the entanglement of nonpolar, rigid primary chains. © 2000 John Wiley & Sons, Inc. J Polym Sci A: Polym Chem 38: 4396–4402, 2000
Keywords: amphiphilic polymer; crosslinked polymer precursor; benzyl methacrylate; polyethylene glycol dimethacrylate; crosslinking

INTRODUCTION

We have been concerned with the mechanistic discussion of 3-dimensional network formation in the free-radical polymerization and copolymerization of multivinyl compounds.[1] In particular, our attention has been focused on the clarification of the reasons for the greatly delayed gelation from Flory–Stockmayer (FS) gelation theory.[2] The primary factor is the significance of the thermodynamic excluded volume effect on the intermolecular crosslinking reaction between the growing polymer radical and prepolymer at an early stage of polymerization. Beyond the theoretical gel point, a secondary factor is related to the intramolecular crosslinking that becomes progressively important with the progress of the polymerization. The latter leads to the restriction of segmental motion of the prepolymer and, moreover, imposes steric hindrance, inducing the significance of the reduced reactivity of prepolymer as a tertiary factor. On the basis of the above mechanistic discussion, we have successfully pursued polymerization conditions in which the actual gel point is close to the theoretical one by removing

the significance of the thermodynamic excluded volume effect and intramolecular crosslinking as the respective primary and secondary factors for the greatly delayed gelation from FS theory.[3-6]

In our preceding article[7] we discussed the crosslinking copolymerizations of benzyl methacrylate (BzMA) with triicosaethylene glycol dimethacrylate $[CH_2=C(CH_3)CO(OCH_2CH_2)_{23}OCOC(CH_3)=CH_2$, PEGDMA-23] because BzMA forms rather rigid, nonpolar primary chains and PEGDMA-23 as crosslinker contains flexible, polar polyoxyethylene units. Thus, the resulting prepolymers (i.e., precursors of the ideal crosslinked polymers) governed by FS theory would probably provide novel amphiphilic polymers. Therefore, BzMA/PEGDMA-23 copolymerizations were conducted under the specified conditions in which the occurrence of a thermodynamic excluded volume effect and intramolecular crosslinking as the primary and secondary factors, respectively, for the greatly delayed gelation in the free-radical monovinyl-divinyl copolymerizations would be reduced. First, the good applicability of FS theory is verified by the comparison of the actual gel point with the theoretical one. Second, the tailed molecular-weight distribution curves are observed with conversion as a result of the exclusive occurrence of an intermolecular crosslinking reaction leading to the ideal network formation governed by FS theory. Third, the applicability of FS theory is supported by both the correlations of the molecular weight versus the elution volume and the root mean square radius of gyration versus the molecular weight, although the molecular size shrinkage of the resulting prepolymers consisting of rather rigid poly(BzMA) chains and flexible polyoxyethylene crosslinkages would be enhanced with conversion as a result of increased crosslinking.

In the present article we extended the above discussion to the preparation and characterization of novel amphiphilic polymers as vinyl-type network-polymer precursors because the preceding article mainly referred to the mechanistic discussion for the copolymerizations containing a small amount (0.03–0.1 mol %) of PEGDMA-23 as a crosslinker. Although a wide variety of amphiphilic polymers were prepared because of their potential importance in applications such as paints, inks, coatings, adhesives, oil recovery, flocculants, drugs, and personal care goods, as well as because of their biological relevance, they are different from the crosslinked polymer precursors of our present interest.

EXPERIMENTAL

The BzMA as a monomer, 2,2'-azobisisobutyronitrile (AIBN) as an initiator, and 1,4-dioxane as a solvent were purified by conventional methods. The PEGDMA-23, (monomer, Kyoeisha Chemical Co., Ltd.) and lauryl mercaptan (LM, chain transfer agent, extrapure reagent commercially available) were used without further purification.

Polymerization was carried out in a glass ampule containing the required amounts of monomers, AIBN, 1,4-dioxane, and LM. The ampule was degased 3 times by the usual freezing and thawing technique under a vacuum, flushed with nitrogen, and then sealed off. It was then placed in a thermostat regulated at 50 ± 0.1 °C. After a predetermined reaction time, the copolymer was precipitated by pouring the reaction mixture into a large excess of chilled methanol containing a small amount of hydroquinone as an inhibitor. The purification of the polymer was done by reprecipitation from a tetrahydrofuran (THF) precipitant system. The gel fraction of the polymer at conversions beyond the gel point was separated by extracting the sol fraction with THF.

The weight-average molecular weight (M_w) of the resulting polymers were measured by size-exclusion chromatography (SEC) using a dual detector system set in the direction of flow, which consisted of a multiangle laser light scattering (MALLS) device and a differential refractometer in sequence. The SEC-MALLS measurements were carried out at 40 °C in THF using a three-column Shodex GPC KF-806L and a two-column KF-807 at polymer concentrations of 0.1–0.5% (w/v) and a flow rate of 1 mL/min. The MALLS device was a DAWN model F (Wyatt Technology Corp.); the laser beam had a wavelength of 632.8 nm and was focused on a 67-μL flow cell. The intrinsic viscosity [η] was determined with an Ubbelohde viscometer at 30 °C.
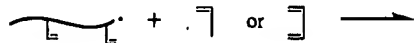
RESULTS AND DISCUSSION
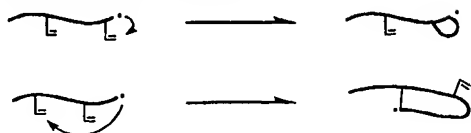
Monovinyl/Divinyl Crosslinking Copolymerization

Figure 1 shows the reaction scheme for the network formation processes in a free-radical monovinyl-divinyl copolymerization, which essentially involves four reactions of a growing polymer radical: intermolecular propagation with two types of monomer; intramolecular cyclization leading to the formation of ring or loop structures;
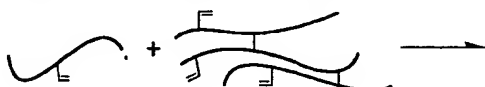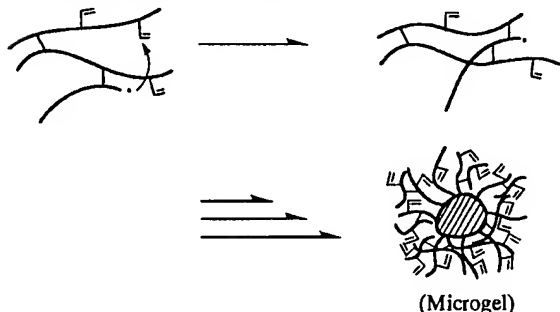
1) Intermolecular propagation with monomer:

2) Intramolecular cyclization:

3) Intermolecular crosslinking with prepolymer:


4) Intramolecular crosslinking:

(Microgel)

Figure 1. A reaction scheme for the network formation processes in the free-radical monovinyl-divinyl copolymerization.

intermolecular crosslinking with the prepolymer to form an effective crosslink, eventually leading to the gel; and intramolecular crosslinking leading to the formation of multiple crosslinks, the locally extensive occurrence of which would induce microgelation. Thus, the network structure of the resulting crosslinked polymer could be designed by controlling the elementary reactions shown in Figure 1: the intermolecular crosslinking is the key reaction for the control of gelation as the formation of a 3-dimensional network of indefinitely large size, whereas the key reaction for the control of the network structure is the intramolecular crosslinking that leads to the formation of multiple crosslinks generating the network structure of the crosslinked polymer. As extreme cases, we depict two typical structures of crosslinked polymers in Figure 2 as an ideal network polymer governed by FS theory and a microgel greatly deviated from the theory, although the structures of the actual crosslinked polymers would be between the two extreme cases. Fur-

thermore, they should change from a rather homogeneous network structure biased toward the ideal network polymer to an inhomogeneous one biased toward the microgel according to the polymerization conditions. In addition, the distribution of inhomogeneity of the network structure would be important for the characterization of the resulting network polymers.

In the preceding article[7] as an extension of our previous works,[3-6] the copolymerization of BzMA was carried out with a rather small amount (0.03–0.1 mol %) of PEGDMA-23 as the crosslinker at a high monomer concentration because, under these conditions, the polymer concentration at the theoretical gel-point conversion becomes high and the content of pendant vinyl groups in the prepolymer is quite small. As a consequence, the thermodynamic excluded volume effect and intramolecular crosslinking would be suppressed. In addition, a small amount of LM as a chain transfer agent was added to keep the

A

B
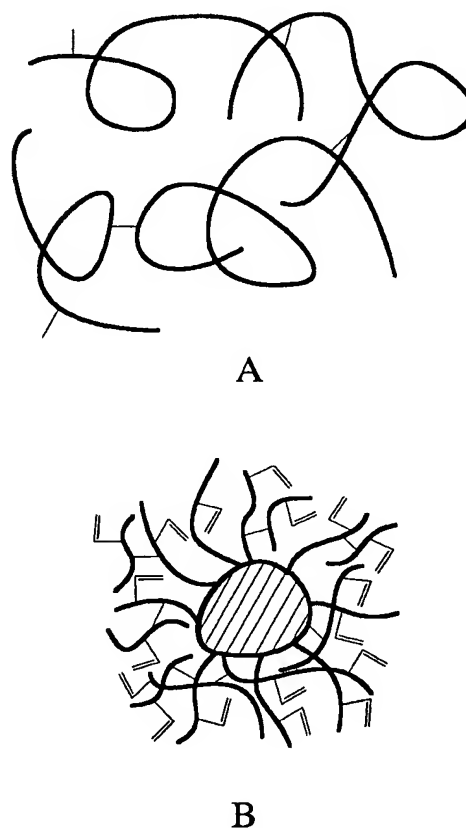
Figure 2. Two extreme structures of crosslinked polymers as (A) an ideal network polymer and (B) a microgel.
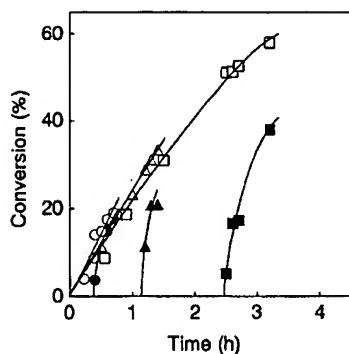
Figure 3. Conversion–time curves for the solution copolymerization of BzMA with 5 mol % of PEG-DMA-23 in 1,4-dioxane at a dilution of 2/3 using 0.04 mol/L of AIBN at 50 °C in the presence of different amounts of LM; [LM]/[total monomer] = (O) 1/200, (△) 1/50, and (□) 1/20. (O, △, □) The total and (●, ▲, ■) gel polymers.

primary chain length constant during polymerization. The commonly observed Trommsdorff effect or gel effect,[8,9] which enlarges the primary chain length with conversion, is suppressed by the addition of a chain transfer agent.

In the present work, a rather large amount of PEGDMA-23 as a crosslinker was used because the balance of the weight percentages of nonpolar and polar components is important for the discussion of the amphiphilicity of the resulting prepolymers. Consequently, intramolecular crosslinking may occur, although the resulting gels are still rather homogeneous as is discussed later.

Deviation from FS Theory

Figure 3 shows the conversion–time curves for the solution copolymerizations of BzMA with 5 mol % (corresponding to 27.5 wt %) of PEG-DMA-23 in 1,4-dioxane at a dilution of 2/3 using 0.04 mol/L of AIBN at 50 °C in the presence of different amounts of LM ([LM]/[total monomer] = 1/200, 1/50, and 1/20). The percentage of gel polymer obtained by the sol–gel separation is also plotted against time in Figure 3. The actual gel point was determined by extrapolating the gel formation curve to 0%. Thus, the conversions at which the gel started to form (i.e., the gel points) were estimated to be 12.4, 26.5, and 49.1% at LM/total monomer concentration ratios of 1/200, 1/50, and 1/20, respectively. The gel point became higher with increasing the added amount of LM as a reflection of reduced primary chain length. In

addition, no gel effect was observed, although the polymerization was accompanied by gelation.

Figure 4 shows the dependence of the M_w on conversion; the primary chain length ($\bar{P}_{w,0}$) was calculated from the $M_{w,0}$ value determined by the extrapolation of each curve to zero conversion. The $\bar{P}_{w,0}$ value thus obtained was then employed to calculate the theoretical gel point according to Stockmayer's equation:[2]

$$\alpha_c = (1/\rho)(\bar{P}_{w,0} - 1)^{-1},$$

where ρ is the fraction of all double bonds residing on the divinyl units in the initial system.

Table I summarizes the results obtained as a comparison of actual gel points with theoretical ones for the copolymerizations of BzMA with 5 mol % of PEGDMA-23 in the presence of different amounts of LM. The actual gel point was quite delayed from the theoretical one for each polymerization system and the deviation (i.e., the ratio of the actual gel point to the theoretical one) became smaller from 6.2 to 4.6 with a decrease in the primary chain length, which was in line with our previous results.[1,10]

Here it should be recalled that in the BzMA/PEGDMA-23 copolymerization[7] the formation of a rather rigid, nonpolar growing chain by the incorporation of BzMA units into the polymer backbone might reduce the occurrence of intermolecular crosslinking reactions with unreacted methacrylic double bonds present at the terminal of polar polyoxyethylene chain. Thus, in spite of the delayed gelation from FS theory as shown in Table I, we may expect the formation of a rather homogeneous A-type network structure compared with an inhomogeneous B-type one (see Fig. 2).
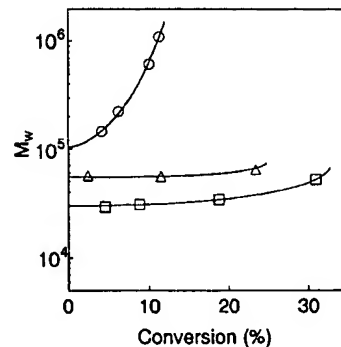
Figure 4. The dependence of the M_w on the conversion (see Fig. 3).

Table I. Comparison of Actual and Theoretical Gel Points in Copolymerization of BzMA with 5 mol % PEGDMA-23

[LM]/[Total Monomer]	$\bar{P}_{w,0}$[a]	Gel Point (%)		Actual Gel Point[d]
		Theor[b]	Actual[c]	Theor Gel Point[b]
1/200	617	1.7	12.4 (9.9)[d]	5.8
1/50	238	4.0	26.5 (21.1)[d]	5.3
1/20	125	8.5	49.1 (39.0)[d]	4.6

The copolymerization was conducted in dioxane at a dilution of 2/3 with [AIBN] = 0.04 mol/L and at 50 °C.

[a] Estimated by SEC-MALLS.

[b] Theoretical gel point: $\alpha_c = (1/\rho)(\bar{P}_{w,0} - 1)^{-1}$.

[c] Obtained on a monomer basis.

[d] Obtained as the vinyl group conversion calculated by assuming equal reactivity of BzMA and PEGDMA-23 vinyl groups.

We tried to check the swelling ratios of the resulting gels obtained just beyond the gel point, because the gel should not swell well if it is the agglomerate of B-type microgels formed through the locally extensive occurrence of intramolecular crosslinking.

### High Swelling Ratio of Gel Obtained Just beyond Gel Point

Figure 5 shows the variation of the swelling ratios of resulting gels with the progress of polymerization beyond the gel point for the solution copolymerizations of BzMA with 5 mol % of PEG-DMA-23 in 1,4-dioxane at a dilution of 2/3 at 50 °C in the presence of different amounts of LM
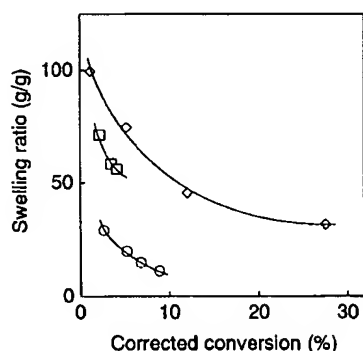
Figure 5. The decrease in the swelling ratio of the resulting gel in THF with the progress of polymerization beyond the gel point [see Fig. 3; [LM]/[total monomer] = (O) 1/200 and (□) 1/20] and the results for (◇) St/m-DVB (99.83/0.17) copolymerization. The conversion in the abscissa is corrected such that the corresponding gel point is 0% of conversion.

([LM]/[total monomer] = 1/200 and 1/20), along with the results for styrene/m-divinylbenzene (St/m-DVB, 99.83/0.17) copolymerization. Here it should be recalled that the ratio of the actual gel point to the theoretical one is 1.3 for St/m-DVB (99.83/0.17) copolymerization.[6] Although the swelling ratios were reduced as gelation progressed, the swelling ratios of the gels obtained just beyond the gel points were extrapolated to be quite high, even for BzMA/PEGDMA-23 (95/5) copolymerizations, although their values were smaller than in St/m-DVB (99.83/0.17) copolymerization as an ideal network formation system. This may demonstrate a rather homogeneous A-type network structure formation in the BzMA/PEGDMA-23 (95/5) copolymerizations.

We attempted to check the amphiphilicity of the resulting gels by measuring their swelling ratios in the mixed solvents consisting of nonpolar t-butylbenzene (t-BB) and polar methanol (MeOH). Figure 6 shows the correlations of the swelling ratios of the resulting gels with the MeOH (vol %) in the mixed solvents for the BzMA/PEGDMA-23 (95/5) solution copolymerizations in the presence of different amounts of LM ([LM]/[total monomer] = 1/200 and 1/20). The gels shrank at both terminals (i.e., in pure t-BB and MeOH) whereas they swelled maximally at about 20 vol % of MeOH. These profiles of the solvent component dependencies of the swelling ratios are characteristic of amphiphilic gels. The swelling ratios of the gels obtained in the BzMA/PEG-DMA-23 (99/1) copolymerization, in which content of the polar component was low, are plotted in Figure 6 for a comparison. The swelling profile was completely different as a reflection of
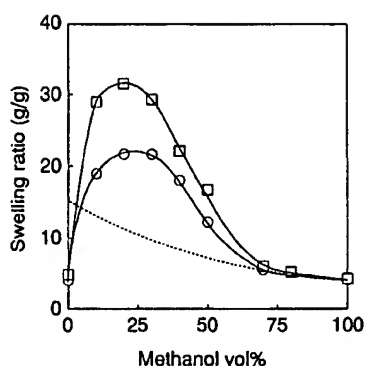
Figure 6. The correlations of the swelling ratio of the resulting gel with the MeOH (vol %) in the mixed solvents consisting of nonpolar t-BB and polar MeOH [see Fig. 3; [LM]/[total monomer] = (O) 1/200 and (□) 1/20] and the results for the (- - -) BzMA/PEGDMA-23 (99/1) copolymerization.

the characteristic nature of the nonpolar BzMA/PEGDMA-23 (99/1) gel (i.e., the highest swelling ratio was observed in pure t-BB), not like amphiphilic BzMA/PEGDMA-23 (95/5) gels. On the basis of the results thus obtained, we roughly depict the conformation of network segments of amphiphilic BzMA/PEGDMA-23 (95/5) gel in t-BB, the t-BB/MeOH (80/20) mixture, and MeOH as shown in Figure 7. The flexible, polar polyoxyethylene units consisting of 23 oxyethylene units shrink in t-BB whereas the rather rigid, nonpolar primary chains mainly consisting of BzMA units shrink in MeOH. In the t-BB/MeOH (80/20) mixture the polar polyoxyethylene units and nonpolar primary chains would both be in a random conformation.

Viscometry Characterization of Resulting Amphiphilic Prepolymers

The BzMA/PEGDMA-23 (95/5) prepolymers obtained just before the gel-point conversions were

In t-BB   In t-BB / MeOH(80/20) mixture   In MeOH
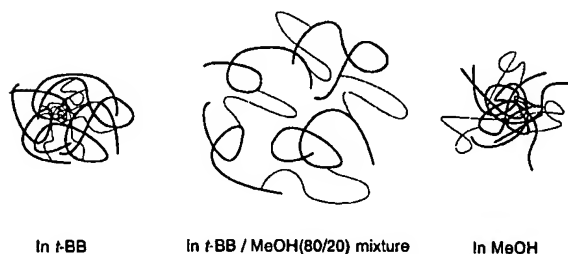
Figure 7. A rough conformational sketch of the network segments of amphiphilic BzMA/PEGDMA-23 (95/5) gel in t-BB, a t-BB/MeOH (80/20) mixture, and MeOH.
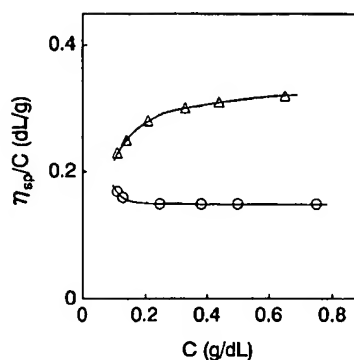
Figure 8. The dependence of the reduced viscosity on the concentration in (O) t-BB and (△) a t-BB/MeOH (80/20) mixture for BzMA/PEGDMA-23 (95/5) prepolymer obtained at [LM]/[total monomer] = 1/20.

then subjected to a viscosity measurement to characterize the amphiphilicity of the resulting prepolymers or crosslinked polymer precursors. Figure 8 shows the dependence of the reduced viscosity on concentration for the BzMA/PEGDMA-23 (95/5) prepolymer obtained at LM/total monomer concentration ratios of 1/20. Here the t-BB and t-BB/MeOH (80/20) mixture were employed as two typical solvents. The viscosities in the t-BB/MeOH (80/20) mixture were quite high compared to those in t-BB, and completely reversed concentration dependencies were observed between both solvents. It is noteworthy here that a crosslinked polymer precursor is essentially a highly branched polymer with loop structures introduced through a intramolecular cyclization and crosslinking reactions, especially when the primary chain length is short. In addition, its molecular-weight distribution is broad and the polymer of higher molecular weight would contribute more significantly to the bulk viscosity of the crosslinked polymer precursor. Thus, the former result would be ascribed to the difference in conformation (see Fig. 7) and the latter to the shrinkage of polar, flexible polyoxyethylene units or to the entanglement of nonpolar, rigid primary chains in t-BB or t-BB/MeOH (80/20), respectively.

CONCLUSION

The free-radical crosslinking copolymerization of BzMA with PEGDMA-23 in the presence of LM as a chain transfer agent was investigated in detail because BzMA forms rather rigid, nonpolar pri-

mary chains and PEGDMA-23 as a crosslinker contains a flexible, polar polyoxyethylene unit; therefore, the resulting prepolymers (i.e., precursors of crosslinked polymers) would be novel amphiphilic polymers. Thus, BzMA was copolymerized with 5 mol % of PEGDMA-23 in the presence of different amounts of LM. The swelling ratios of the gels obtained just beyond the gel points were extrapolated to be quite high; this may demonstrate a rather homogeneous A-type network structure formation in the BzMA/PEGDMA-23 (95/5) copolymerizations. The amphiphilicity of the resulting gels was checked by measuring their swelling ratios in the mixed solvents consisting of nonpolar t-BB and polar MeOH; the solvent component dependencies of the swelling ratios are characteristic of amphiphilic gels.

The BzMA/PEGDMA-23 (95/5) prepolymers obtained just before the gel-point conversions were then subjected to a viscosity measurement using t-BB and a t-BB/MeOH (80/20) mixture as solvents in order to characterize the amphiphilicity of the resulting prepolymers as crosslinked polymer precursors. The viscosities in t-BB/MeOH (80/20) mixture were quite high compared to those in t-BB, and completely reversed concentration dependencies were observed with the solvents. These were discussed by considering the difference in conformation and the shrinkage of polar, flexible polyoxyethylene units or the entanglement of nonpolar, rigid primary chains.

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Analysis of Polymers

AN INTRODUCTION

by

T. R. CROMPTON

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7
Fractionation and molecular weight

POLYMERS normally do not consist of a particular molecule with a unique molecular weight, but rather are a mixture of molecules with a molecular weight range which follows a distribution. With some types of polymers the picture is further complicated by the appearance of what are known as crosslinks. These are chemical bonds which link one polymer chain to another. Crosslinking will, therefore, increase the molecular weight of a polymer and, incidentally, decrease its solubility in organic solvents. These are some of the features which make it possible to produce for a given polymer, say polypropylene, a range of grades of the polymer, each with different physical properties and end-uses and each characterized by a different molecular weight distribution curve and degree of crosslinking. The factors which control these parameters in a polymer are complex, and are linked with the details of the manufacturing process used. They will not be discussed further here. The measurement of the molecular weight is a task undertaken in its own right by polymer chemists, and is concerned with the development of new polymers and process control in the case of existing polymers. Additionally, however, it is necessary to separate a polymer not into unique molecules each with a particular molecular weight, but into a series of narrower molecular weight distribution fractions. This is required in order to obtain a more detailed picture of the polymer structure and these separated fractions may be required for further analysis by a wide range of techniques.

In the simplest case, discussed in section 7.1 below, it is required simply to separate, for example, the total gel fraction (i.e. crosslinked material) of a polymer from the total soluble fraction (non-crosslinked material). This is typified in the example discussed below on the separation of polystyrene into its gel and soluble fractions. In a more complicated case it may be required to carry out a separation of the original polymer into a series of fractions each with a narrower molecular weight distribution than the parent polymer. These methods are usually based on fractionation techniques, in turn based on solvent gradient fractionation or thermal gradient fractionation as discussed in section 7.2. Finally, there is the case where it is required to determine the molecular weight distribution of the polymer. Depending on the type of polymer being examined many methods exist for carrying out these measurements (section 7.3) based on

gel permeation chromatography or size exclusion chromatography, to mention new techniques. Techniques that have been in existence for longer include turbidimetric methods, osmometry, viscometry, light-scattering methods, and sedimentation velocity.

7.1 Measurement of crosslinked gel content

Method for soluble–insoluble separations

A good example of this is the separation of the two fractions from a styrene–butadiene–acrylonitrile polymer and the determination of the monomer units in the separated fractions.

To remove non-polymer additives the polymer is dissolved (or dispersed) in chloroform. This solution is slowly poured into an excess of stirred methanol to reprecipitate the polymer and leave the soluble non-polymer additives in a clear chloroform–methanol phase which can be separated from the polymer by filtration. The polymer is then washed with methanol and vacuum-dried.

Contact with methyl ethyl ketone followed by high-speed centrifuging is an excellent method of separating the two fractions. Table 53 reports

TABLE 53   Determination of monomer units in ABS terpolymers

Determined	Cycolac T 1000 natural nibs	Cycolac H 1000 natural nibs	Kralastic MH nibs
Analysis of additive free polymer			
Butadiene (%)*	20.5	28.6	19.1
Acrylonitrile (%)†	23.8	20.9	20.9
Styrene (%)‡	54.0	48.5	
	(total = 98.3%)	(total = 98.0)	
Analysis of insoluble fraction			
Insolubles in polymer (%)	56.0*	51.5**	11.0
Butadiene (%)	30.8	31.2	49.9
Acrylonitrile (%)	22.1	20.6	10.7
Styrene (%)	48.0	48.0	—
	(total = 100.9%)	(total = 99.8%)	
Analysis of soluble fraction			
Solubles in polymer (%)	44.0	48.5	—
Butadiene (%)	10.3	7.0	13.9
Acrylonitrile (%)	27.6	28.7	21.5
Styrene	62.0	64.0	61.0
	(total = 99.9%)	(total = 99.7%)	(total = 96.4%)

* Iodine monochloride method.
† Kjeldahl method.
‡ Infrared method.

complete gel and soluble fraction analysis carried out on various ABS polymers. In both the whole ABS polymer and in its soluble and insoluble fractions the sum of the determined constituents usually adds up to 100 ± 2%.

Methods have been described for the determination of gel in PVC,[698-700] vinyl chloride–propylene copolymer,[700] polybutadiene–polyisoprene copolymer styrene–butadiene copolymer, acrylonitrile–butadiene, copolymer polyacrylonitrile[699] and styrene–acrylonitrile copolymer.[701]

7.2 Types of polymer fractionation procedures

7.2(a) Fractionation of polymers based on molecular weight

The time-consuming and laborious nature of the earlier fractionation procedures is illustrated well by the work of Nakajima[702] on the fractionation of polyethylene and its thermally degraded products, involving extraction with boiling hydrocarbons with increasing boiling points between 45°C and 95°C, and on the fractionation of polypropylene.[703] It was necessary to extract the polymer using a Soxhlet apparatus with 17 different hydrocarbon fractions based on normal paraffins with different boiling temperatures in the range from 35°C to 135°C. The extreme laboriousness of such procedures is self-evident.

Fractional extractions of polymers by the column technique is no less laborious. Two types of column extraction procedure are known. Gradient elution fractionation is achieved at a given temperature by making use of solvents with gradually increasing solvent power, or the increasing temperature fractionation is performed with a given solvent at increasing temperatures. According to the findings on column techniques by Wijga et al.,[704] the gradient of the polymer separates fractions according to molecular weight, whereas the increasing temperature method fractionates the polymer mainly according to tacticity.

7.2(b) Gradient elution with solvents of increasing solvent power at constant temperature

The polymer is packed in a column and a solvent mixture passed down the column. Initially the solvent is a poor one for the polymer. Then increasing proportions of a better polymer solvent are incorporated in the solvent mixtures utilizing a gradient elution technique. A series of fractions is thus obtained, containing different molecular weight fractions of the original polymer. Methods have been described for the large-scale elution fractionation of ethylene–propylene copolymers,[705] methyl methacrylate–styrene copolymers,[706] polyethylene,[707] and polypropylene.[708]

7.2(c) Increasing (or decreasing) temperature fractionation

When a solid polymer packed in a column is contacted with a continuing flow of solvent in which it has a limited solubility at room temperature then, as the temperature of the column is raised in a controlled programme, fractions of the polymer with different tacticities will progressively dissolve. Collection of portions of the column eluate at various temperatures will provide a series of fractions.

Akutin et al.[708] have shown that by a thermal precipitation method the molecular weight distribution of low-density polyethylene could be deduced from the precipitation curves using simple calculations. Ogawa and Hoshino[709] compared fractionations of isotactic polypropylene by using temperature and solvent gradient methods. Comparison of results agreed fairly well on fractionation of polyethylene–polypropylene blends between hypothetical calculations and experimental data by solvent gradient method.[710]

7.2(d) Fractionation by polymer freezing

Polystyrene dissolved in benzene has been fractionated by slowly freezing the solutions with dry ice and alcohol. A more detailed treatment of this method is given by Loconti and Cahill.[711,712] The polymer in the first frozen-out portions was of higher molecular weight than later. Ruskin and Parravano[713] were able to fractionate polymer dissolved in cyclohexane by both the zone-melting and freezing techniques.

Bryson et al.[714] investigated the fractionation of polystyrene by slow freezing of dilute benzene solutions of the polymer using ice-water mixtures instead of dry ice-alcohol. Bryson et al.[714] concluded that no fractionation of the polymer occurs according to molecular weight from benzene solutions.

7.2(e) Precipitation chromatography

In this technique the polymer is dissolved in a solvent and then gradual additions are made of a non-solvent to the polymer. The polymers precipitated after each non-solvent addition are separately collected. An example is the case of vinylchloride–vinyl acetate copolymers using solvent–non-solvent systems such as acetone–methanol, acetone–heptane and tetrahydrofuran–water.[715]

Precipitation with methanol from benzene solution has been used to fractionate methacrylic acid–styrene copolymer,[716] polychloroprene,[717,718] polybutadiene,[717,718] and polyisoprene.[717,718] Other solvent–non-solvent systems that have been used include nitrobenzene–tetrachloroethane (polyethylene tetraphthalate[719]) and ethylene carbo-

Experiments in Polymer Science

EDWARD A. COLLINS

JAN BAREŠ

FRED W. BILLMEYER, JR.

/9 3

EXPERIMENT 30.   SWELLING OF NETWORK POLYMERS

A. Introduction

This experiment is designed to determine the number of effective network chains (crosslinks) per unit volume of polymer. Two useful pieces of information are obtained: The resistance of the polymer to the solvent, and the crosslink density of the polymer. The time for this experiment will vary depending upon the crosslinking level. It can be carried out in two hours total time but may require an elapsed time of 24 hours.

B. Principle

Swelling is the first step in the solubilization of a polymer. The degree of swelling depends upon the polymer-solvent interaction parameter χ_1 and the molecular weight of the polymer. In the case of a crosslinked polymer, solubilization cannot take place, and an equilibrium degree of swelling is attained. The swelling experiment can be run gravimetrically or volumetrically; for this experiment, the gravimetric technique is employed. Knowledge of the value for the polymer-solvent interaction parameter χ_1 allows the crosslink density per unit volume of polymer or the molecular weight between crosslinks to be calculated. Pinner (1961) describes a similar experiment, his Exp. C.3.3.

C. Applicability

This technique is applicable to most crosslinked polymers provided a suitable swelling solvent can be found. The method works best for low crosslink densities, since the fewer the crosslinks, the greater the swelling.

D. Precision and Accuracy

The precision of this technique can be such as to detect small amounts of swelling (0.2%) with a reproducibility of 1%. Accuracy has little meaning in this experiment. See steps M-1 to M-3.

E. Safety Considerations

CARE MUST ALWAYS BE TAKEN TO USE ORGANIC SOLVENTS IN WELL-VENTILATED AREAS AWAY FROM SOURCES OF FLAME OR SPARKS. AVOID BREATHING FUMES OR EXCESSIVE CONTACT OF SOLVENT WITH SKIN. SAFETY GLASSES MUST BE WORN AT ALL TIMES IN THE LABORATORY.

F.   Apparatus

1.   Analytical balance.
2.   Stoppered flasks, wide mouth, any convenient size.
3.   Filter paper.

G.   Reagents and Materials

1.   Crosslinked polymers prepared in Exp. 8, or suitable substitute such as vulcanized rubber.
$\longrightarrow$ solvent 2.   Toluene, reagent grade.

H.   Preparation

The samples should be in the form of sheets which can be cut with scissors or razor blade.

I.   Procedure

1.   Cut three specimens weighing approximately 2 g each, accurately weigh each specimen, and place it in a stoppered flask containing enough toluene to cover the specimen.
2.   Periodically remove the specimen, blot it dry with filter paper, and rapidly weigh it. (*Note:* Work rapidly to avoid loss of solvent by deswelling and evaporation, causing the sample weight to drift downward.) Repeat until the sample reaches its equilibrium degree of swelling. Use the final constant weight in the calculations to follow.

J.   Fundamental Equations

$$V_s = w_0/\rho_2 + (w_s - w_0)/\rho_1 \tag{10-37}$$

$$c = V_s w_0/\rho_2 \tag{10-39}$$

$$M_x = - v_1\rho_2(c^{1/3} - c/2) \ / \ [\ln(1-c) + c + \chi_1 c^2] \qquad \text{(from 10-38)}$$

K.   Calculations

1.   For each sample, calculate the equilibrium volume after swelling using Eq. 10-37, the equilibrium concentration of polymer in the swollen gel using Eq. 10-39, and the average molecular weight between crosslinks, M_x, using Eq. 10-38, and taking $\chi_1 = 0.44$ for polystyrene in toluene (Huggins 1943).

L. Report

1. Describe the experiment in your own words.
2. Report the data in tabular form.
3. Explain the cause of variability in the results.
4. Answer the following questions:

    a. What effect does solubility of the polymer have on the result?

    b. How can the interaction parameter, χ_1, be determined (see Chap. 7A)?

M. Comments

1. The presence of any uncrosslinked material in the polymer network, which may dissolve and change the concentration, can be a source of error. A sample of the solution should be tested for dissolved polymer.
2. It should be recognized that inherent in the analysis are the experimental and theoretical difficulties encountered with the Flory-Huggins thermodynamic theory, upon which the development of Eq. 10-38 is based.
3. A variation of this experiment is to determine the cohesive energy density, as described by Bristow (1958*a*, *b*).

N. General References

Chap. 10E; *Textbook*, Chap. 2A; Flory 1953; Treloar 1958; Ellis 1963*a*, *b*; Miller 1966, Chap. 7; Smith 1968.

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EXPERIMENT 31.   PERMEABILITY OF POLYMERS TO GASES

A.   Introduction

In this experiment, the rate of permeability of carbon dioxide
through a polymer film is determined at different pressures. This
experiment can be carried out in 3 hours.

B.   Principle

The rate of gas permeation through a film is measured by deter-
mining the volume of gas permeating through the film under a pressure
differential. A high gas pressure is applied on one side of the mem-
brane under study, and the permeated gas is allowed to expand on the
opposite side against atmospheric pressure. The volume of the per-
meating gas is measured as a function of time by following the dis-
placement of a short column of mercury in a glass capillary. A
standard method for this experiment is described in ASTM D 1434.

C.   Applicability

This method is applicable to most polymers which can be obtained
as suitable films.

D.   Precision and Accuracy

The precision of this experiment varies with the permeability,
since it depends on a volume measurement. In practice, it is found
that for high permeabilities, a precision of ±5% can be attained,
while for low permeabilities the precision is closer to ±15%. Abso-
lute accuracy has no meaning in this experiment.